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Interlaboratory Evaluation of SW-846 Methods 7470 and 7471 for the Determination of Mercury in Environmental Samples

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INTERLABORATORY EVALUATION OF SW-846 METHODS 7470 AND 7471 FOR THE DETERMINATION OF MERCURY IN ENVIRONMENTAL SAMPLES

by

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The EPA protocols for SW-846 Methods 7470 and 7471 are cold-vapor atomic absorption spectrometric (CV-AAS) methods for the determination of mercury in aqueous and solid environmental samples. In continuation of a previous single-laboratory study in which a revised more sensitive mercury CV-AAS method for environmental analyses was evaluated, the revised CV-AAS method has been subjected to an interlaboratory study. The revised CV-AAS system, operated in an open configuration, incorporates a dedicated gas sparging bottle for reduction-aeration and an on-line amalgamation/thermal desorption step. With these modifications, the CV-AAS method provides increased sensitivity and also alleviates nonspecific background absorption interferences so that instrumental background correction is not required. The analytical results reported by the collaborating laboratories were statistically examined. In general, the results indicate that the amalgamation CV-AAS method currently is not sufficiently rugged for routine use but, when properly implemented by proficient laboratory personnel, may serve as an alternative approach to the recirculating CV-AAS method described in the current EPA protocols.

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ABSTRACT

The EPA protocols for SW-846 Methods 7470 and 7471 are cold-vapor atomic absorption spectrometric (CV-AAS) methods for the determination of mercury in aqueous and solid environmental samples, respectively. In continuation of a previous single-laboratory study in which a more sensitive mercury CV-AAS method for environmental analyses was evaluated, the revised CV-AAS method has been subjected to an interlaboratory study. The revised CV-AAS system, operated in an open configuration, incorporates a dedicated gas sparging bottle for reduction-aeration and an on-line amalgamation/thermal desorption step. With these modifications, the CV-AAS method provides increased sensitivity and also alleviates nonspecific background absorption interferences so that instrumental background correction is not required.

Silver-wool amalgamation cells, mercury stock standard and spiking solutions, a deionized water sample with spiking instructions, a coal fly ash reference material, and instructions for analysis by the amalgamation CV-AAS method were sent to 18 participating laboratories having prior experience with the current EPA protocols for Methods 7470 and 7471. Ten of the 18 laboratories were then invited to participate in a more rigorous collaborative study. To evaluate the revised Method 7470, three aqueous sample types were analyzed: ground water, waste water, and dilute nitric acid. To evaluate the revised Method 7471, three solid sample types were analyzed: marine sediment, incinerator fly ash, and municipal sewage sludge. Some of the samples were designated for spiking with inorganic or organic mercury and also with copper, a potential interferent.

The analytical results reported by the collaborating laboratories were statistically examined in an attempt to characterize the overall accuracy, precision, and ruggedness of the amalgamation CV-AAS method. In general, the interlaboratory results indicate that the amalgamation CV-AAS method currently is not sufficiently rugged for routine use but, when properly implemented by proficient laboratory personnel, may serve as an alternative approach to the recirculating CV-AAS method described in the current EPA protocols. To fully realize the analytical benefits of the amalgamation CV-AAS method and to obtain accurate and precise data, a complete appreciation of the integral factors for successful trace analyses is essential, and a high level of sophisticated operation and operator skill is required.

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SECTION 1

INTRODUCTION

Publication SW-846, entitled "Test Methods for Evaluating Solid Waste," by the Office of Solid Waste and Emergency Response of the U. S. Environmental Protection Agency provides chemical and physical methods for the characterization of waste materials regulated under the Resource Conservation and Recovery Act (RCRA).[1] Included in the chemical methods are two analytical protocols for the determination of mercury in environmental waste samples by cold-vapor atomic absorption spectrometry (CV-AAS). The EPA protocols for SW-846 Methods 7470 and 7471 are intended for mercury determinations in aqueous and solid waste samples, respectively.

Because of the concern for mercury as a potential hazardous pollutant in environmental wastes, the EPA protocols for mercury are under review. In a previous single-laboratory study,[2] the EPA protocols for SW-846 Methods 7470 and 7471 were evaluated and revised to improve analytical performance. The methods were evaluated using aqueous and solid environmental samples of homogeneous and known compositions in order to assess accuracies and precisions of the methods without introducing uncertainties due to sample heterogeneities.

The results of the single-laboratory study[2,3] indicated, in general, that the digestion procedures were satisfactory for the samples analyzed; only minor revisions that would improve, clarify, or increase the flexibility of the digestion procedures were recommended. The recirculating CV-AAS method described in the current EPA protocols was found to be adequate only for mercury determinations in samples of relatively high mercury concentrations. However, the recirculating CV-AAS method was inadequate for mercury determinations in samples of low mercury levels because of its relatively poor sensitivity. Moreover, interferences which were due to nonspecific absorption of primary mercury radiation by vapors of organic compounds (benzene and methyl ethyl ketone) degraded the accuracy of the recirculating CV-AAS method.

Significant modifications of the cold-vapor apparatus were recommended and evaluated to overcome the analytical limitations of the recirculating CV-AAS method. Instrument detectability was improved 10-fold by collectively using a gas sparging bottle as a dedicated reduction-aeration vessel and silver-wool amalgamation in the CV-AAS system operated in an open configuration. The modified CV-AAS method, with the incorporation of these three instrument modifications, was designated amalgamation CV-AAS. Although the individual contributions of the three instrument modifications were not determined, the amalgamation step provided much of the overall increase in sensitivity. The on-line amalgamation/thermal desorption process of the modified CV-AAS system also effectively eliminated interfering water and organic matrix vapors prior to the mercury absorption

measurement so that an instrument without dynamic background correction capabilities could be used. Good accuracy and precision were obtained with the amalgamation CV-AAS system for the analyses of four reference sediment materials.

The objective of this project was to conduct an interlaboratory evaluation of the revised EPA protocols for the determination of mercury in environmental samples. The mercury protocols to be evaluated included minor revisions in the digestion procedures of Methods 7470 and 7471, and quantification of mercury in the sample digests by the amalgamation CV-AAS method.[2,3] The interlaboratory study was conducted in three phases: (1) Phase I - fabrication and testing of the silver-wool amalgamation cells and characterization of selected interlaboratory study samples by the lead laboratory, (2) Phase II - preliminary evaluation of the technical capabilities of the participating laboratories to utilize the amalgamation CV-AAS method for determining mercury in a coal fly ash reference material and in deionized water spiked with inorganic mercury, and (3) Phase III - evaluation by the qualifying laboratories of the amalgamation CV-AAS method for the determination of mercury in a marine sediment reference material and in representative aqueous and solid waste samples. The test samples contained concentrations of endogenous mercury or were spiked with concentrations of inorganic or organic mercury that were in the optimal range of the amalgamation CV-AAS method. A statistical analysis of the mercury concentration data submitted to Battelle was conducted in an attempt to characterize the interlaboratory accuracy, precision, and ruggedness of the amalgamation CV-AAS methods.

SECTION 2

CONCLUSIONS

The results of this interlaboratory study indicate that only a few of the collaborating laboratories demonstrated proficiency in incorporating the silver-wool amalgamation apparatus into their CV-AAS systems within a relatively short learning period. These laboratories reported calibration slopes in an acceptable range based on Battelle's experience with the amalgamation CV-AAS method. Only a few of the laboratories were able to perform accurate and precise measurements on both aqueous and solid environmental samples.

A statistical treatment of the interlaboratory results indicates that the amalgamation CV-AAS method currently lacks sufficient ruggedness to be successfully used by analytical laboratories for routine testing but, when properly implemented by proficient laboratory personnel, it may serve as an alternative to the recirculating CV-AAS method described in the current EPA protocols of Methods 7470 and 7471. However, to fully realize the analytical benefits of the amalgamation CV-AAS method and to obtain accurate and precise data, a complete appreciation and awareness of the critical factors affecting successful trace analyses are essential, and a high level of sophisticated operation and operator skill is required. Moreover, because of the increased sensitivity of the amalgamation CV-AAS method, improved analytical techniques and the use of high-purity reagents are required to minimize mercury contamination that would not be a problem when using the recirculating CV-AAS method with samples of higher mercury concentrations.

To achieve better results, many of the laboratories reported that they had to modify the operating parameters of the silver-wool amalgamation apparatus from those specifically described in the revised protocols. This may have been necessary when the silver-wool amalgamation apparatus was not assembled and configured properly according to the directions in the protocols, or when the amalgamation apparatus had to be reconfigured to fit a specific commercial or customized CV-AAS system. The different operating conditions used by some laboratories may have contributed to the high dispersion in the amalgamation CV-AAS data submitted to Battelle.

Most of the comments from the collaborating laboratories addressed the increased sensitivity and the longer analysis time of the amalgamation CV-AAS method. Many laboratories recognized the need for higher operator skill and the importance of the need for high-purity reagents to minimize mercury contamination. The benefit of an amalgamation CV-AAS method with increased sensitivity but at the expense of longer analysis time was challenged by some laboratories from a business economics viewpoint; the longer analysis time would increase sample analysis costs to the laboratory that would have to incur the additional costs or charge higher analysis fees to the customer. Although the faster recirculating CV-AAS method was considered adequate for the majority of their samples, other laboratories expressed special needs for the increased sensitivity of the amalgamation CV-AAS

method and indicated that it would be valuable in research and for difficult analysis problems. Some laboratories expressed enthusiasm about the amalgamation CV-AAS method and indicated that they plan to incorporate this method into their laboratory operations for additional flexibility. The extent of time and cost constraints for adapting the amalgamation CV-AAS method to a specific sample workload may be influenced by whether the emphasis of the analytical laboratory is on commercial testing or on research, development and specialty problems in a support function of a larger organization.

SECTION 3

RECOMMENDATIONS

The results of this interlaboratory study, in conjunction with the results of the previous single-laboratory study, indicate that the recirculating CV-AAS method and the amalgamation CV-AAS method have distinct analytical advantages for the determination of mercury in environmental waste samples. However, until its ruggedness is improved, the amalgamation CV-AAS method is not suitable for routine testing by most analytical laboratories. Battelle recommends that the amalgamation CV-AAS method would best serve the analytical community as an alternative method for the determination of trace mercury concentrations in those complex sample types which can not be routinely analyzed by the current recirculating CV-AAS method. Specifically, Battelle recommends that the CV-AAS methods be used to characterize waste samples for mercury as described below:

(1) The current EPA protocols for the recirculating CV-AAS method should be used for analyses when the threshold concentration value for mercury is relatively high and when the samples do not contain volatile organic compounds that could cause nonspecific absorption interferences.

(2) The amalgamation CV-AAS method should be used for the analyses of samples containing low mercury concentrations which can not be easily determined by the recirculating CV-AAS method.

(3) The amalgamation CV-AAS method should be used for the analyses of samples containing volatile organic compounds which will cause nonspecific absorption interferences and inaccurate results with the recirculating CV-AAS method.

Because of the greater sensitivity and the more sophisticated apparatus of the amalgamation CV-AAS system, Battelle emphasizes that the laboratory analysts be properly trained and that they demonstrate proficiency with the amalgamation method before initiating regulatory analyses for mercury.

SECTION 4

MATERIALS AND METHODS

INSTRUMENTATION

The amalgamation CV-AAS system used in Phase I is identical to the system previously used in the single-laboratory study.[2,3] The schematic diagram of the amalgamation CV-AAS system is shown in Figure 1. The operating procedures and instrument parameters are the same as those used in the single-laboratory study except for the primary mercury radiation source used in the atomic absorption spectrophotometer. In the present study, a mercury electrodeless discharge lamp (EDL), supplied with 5 watts of radio-frequency power, was employed instead of the mercury hollow cathode lamp (HCL). The greater spectral intensity of the 253.7-nm resonance line from the EDL allows a lower gain setting to be used for the photomultiplier tube (PMT) detector resulting in a higher signal-to-noise ratio. The relative sensitivities, or slopes, of the calibration curves for the two mercury spectral-line sources are similar.

The amalgamation cell is positioned in the CV-AAS system as shown in Figure 1. Mercury vapor evolved from the reduction-aeration cell is trapped and concentrated by amalgamation on the silver-wool plug positioned in the center of the amalgamation cell. After the reduction-aeration and the on-line amalgamation steps are completed, mercury is desorbed from the silver wool by resistance heating to approximately 500°C. Heat is supplied by applying approximately 20 volts of power to the Chromel A wire windings. The mercury vapor is transported via a nitrogen-gas purge into the absorption cell, and the maximum peak absorbance is recorded. The geometry of the absorption cell used in the single-laboratory and interlaboratory studies was satisfactory although no attempts were made to optimize it for sensitivity. By using the parameters and experimental conditions described in the revised protocols, the appearance time of the mercury peak on the strip-chart recorder with a 1-second time constant is approximately 17 seconds; the maximum peak absorbance occurs between 25 and 30 seconds after heating of the silver-wool plug is initiated.

Four operating parameters of the amalgamation CV-AAS system were optimized and tested for ruggedness in the single-laboratory study.[2,3] These parameters included the nitrogen purge-gas flow rate, the time required for the silver-wool concentration of mercury, the Variac voltage setting for thermal desorption, and the mass of the silver wool. The optimized values for these parameters were used in interlaboratory study.

The timing of the amalgamation and desorption events are especially critical for maximum precision. Based on Battelle's experience, the timing should be reproducible to within a few seconds. A stopwatch is conveniently used to consistently monitor all timing events in the method to insure maximum reproducibility for within-day and day-to-day analyses.

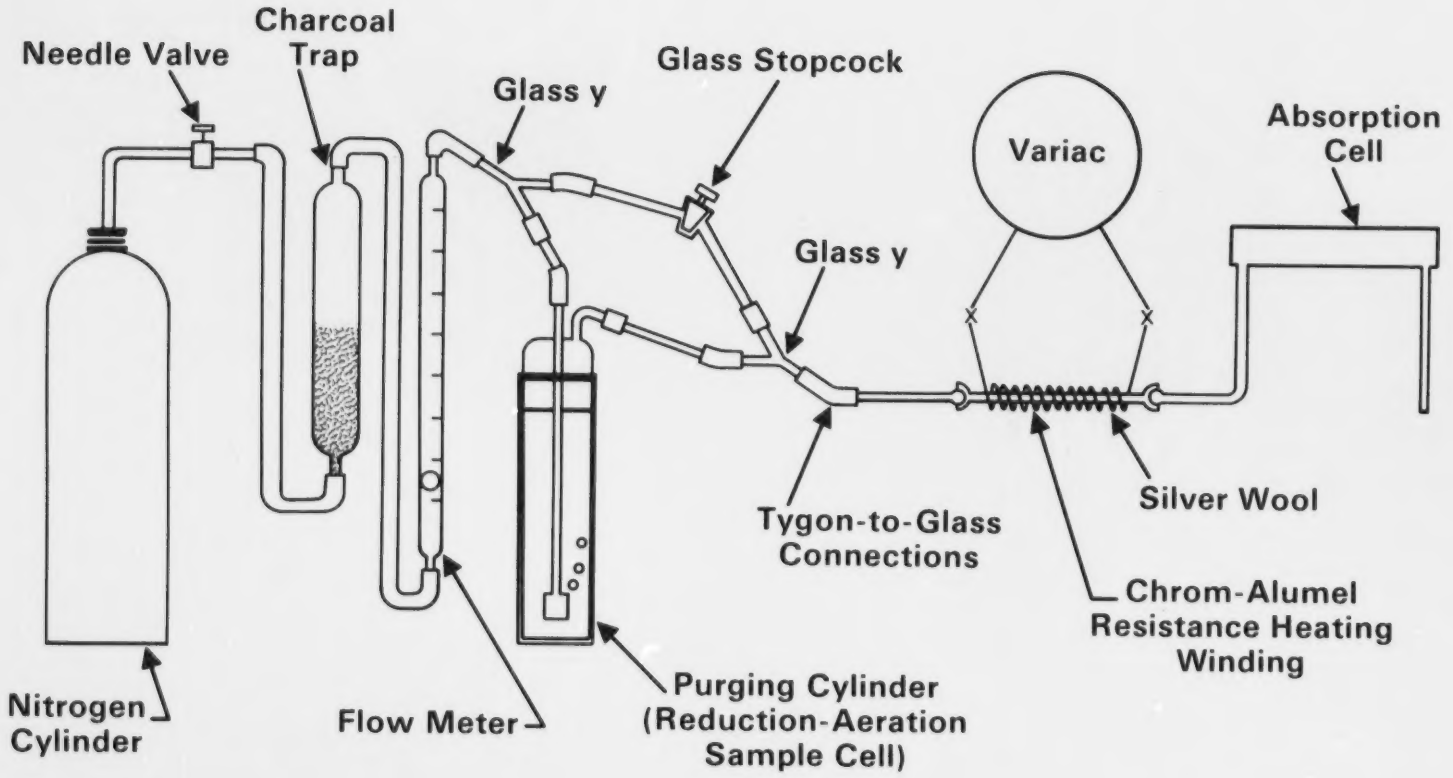

Figure 1. Schematic diagram of the amalgamation CV-AAS system.

In addition to residual vapors resulting from matrix components that survive the digestion procedure, water vapor evolved during the reduction-aeration step may absorb the primary mercury radiation and produce nonspecific absorption interferences. The amalgamation/thermal desorption process has been demonstrated to successfully eliminate interfering water and organic vapors prior to the mercury absorption measurement without compromising the instrument detection limit.[2,3] Although continuum-source background correction should also provide accurate compensation for such vapor interferences, the increased noise level in most of the older atomic absorption systems when operated in the background-correction mode degrades the detection limit. This effect has been previously discussed in greater detail.[2,3] An additional benefit of amalgamation CV-AAS is that the method can be successfully implemented even by using an atomic absorption instrument that is not equipped with a dynamic background-corrector accessory.

AMALGAMATION CELLS

To minimize experimental variability, all of the mercury amalgamation cells used in this study were manufactured, assembled, and tested by Battelle staff. The amalgamation cell with ball-joint connection adapters allowed it to be fitted to commercial cold-vapor mercury accessories. Twenty-three amalgamation cells were constructed, according to the design and specifications in Figure 2, by Battelle glassblowers. The amalgamation cell, with an overall length of 105 mm, consists of ST 12/5 male and female ball joints annealed to opposite ends of Pyrex glass tubing (5 mm i.d.). A silver-wool plug (Fisher Scientific Company, Fair Lawn, NJ) of 0.7 g, with a mass uncertainty of 0.05 g, is inserted into the Pyrex tube and then compacted into a cylinder having approximate dimensions of 5 mm diameter and 20 mm length. This is facilitated by using two narrow stainless steel rods which are directed through the two ends of the Pyrex tube; the silver wool is compacted within the centermost part of the tube length so that it is snug within the tube and so it will not easily be dislodged. A 92-cm length of 22-gauge Chromel A wire (Fisher Scientific Company, Fair Lawn, NJ) is wrapped around the Pyrex tubing, providing 30 windings and a resistance of 22 ohms/ft. This wire-wrapping provides uniform heating over a region approximately three times longer than the silver-wool plug. The 0.7-g plug of silver wool compacted into a cylinder under these conditions quantitatively amalgamates mercury vapor at a nitrogen carrier-gas flow rate of 0.55 L/min with no apparent buildup of leak-inducing backpressure.

REAGENTS

Deionized water with a minimum electrical resistivity of 14 megohm-cm (The Barnstead Company, Division of Sybron Corporation, Boston, MA) or equivalent; deionized water with a minimum electrical resistivity of 1 megaohm-cm (Peck Water Systems Corporation, Canton, OH) served as the inlet source for the Sybron/Barnstead deionization unit.

Hydrochloric acid, HCl, concentrated (37 percent, 12 Normal), FW 36.5, "Baker Ultrex" grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

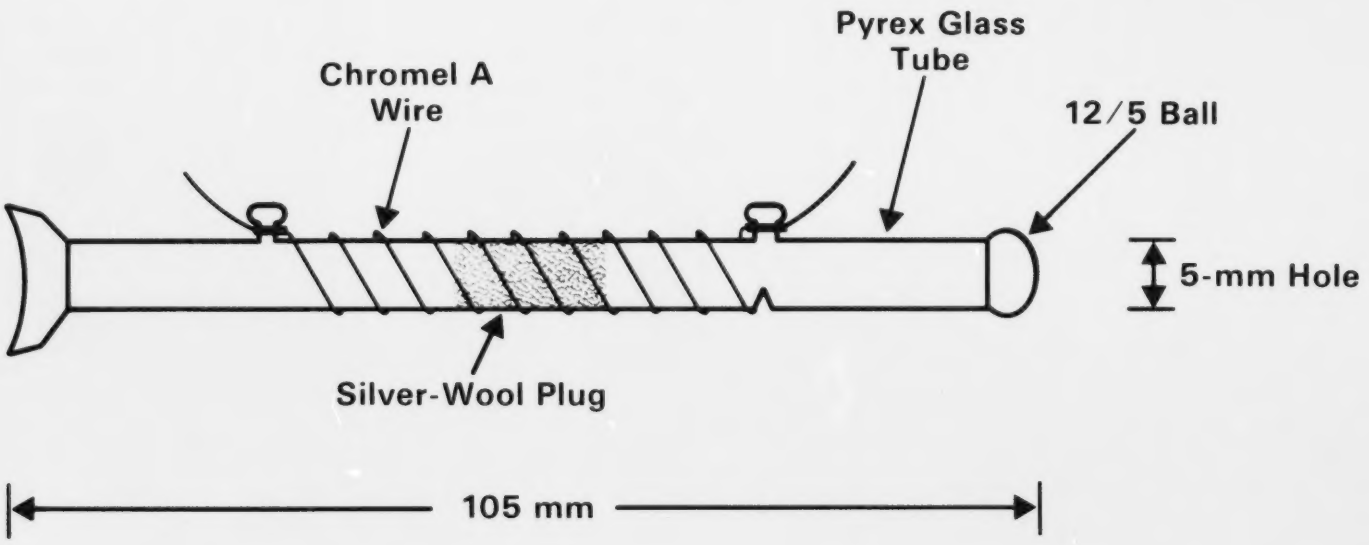

Figure 2. Schematic diagram of the silver-wool amalgamation cell.

Nitric acid, HNO_3, concentrated (70 percent, 16 Normal), FW 63.0, "Baker Ultrex" grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

Nitric acid, 1-percent (v/v) solution: Prepared by carefully mixing 1 volume of concentrated nitric acid with 99 volumes of deionized water.

Sulfuric acid, H_2SO_4, concentrated (96 percent, 36 Normal), FW 98.08, analytical reagent grade (Mallinckrodt, Inc., Paris, KY) or equivalent.

Aqua regia: Prepared immediately before use by carefully adding three volumes of concentrated hydrochloric acid to one volume of concentrated nitric acid.

Hydroxylamine hydrochloride, $NH_2OH \cdot HCl$, FW 69.49, "Baker Analyzed" reagent grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

Sodium chloride, NaCl, FW 58.44, "Baker Analyzed" reagent grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

Sodium chloride-hydroxylamine hydrochloride solution: Prepared by dissolving 60 g sodium chloride and 60 g hydroxylamine hydrochloride in deionized water in a 500-mL volumetric flask, and by diluting to calibrated volume with deionized water.

Potassium permanganate, $KMnO_4$, FW 158.04, "Baker Analyzed" ACS reagent grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

Potassium permanganate, 5-percent (w/v) solution: Prepared by dissolving 50 g potassium permanganate in approximately 500 mL deionized water in a 1-L volumetric flask, and by diluting to calibrated volume with deionized water.

Potassium persulfate, $K_2S_2O_8$, FW 270.32, "Baker Instra-Analyzed" ACS reagent grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

Potassium persulfate, 5-percent (w/v) solution: Prepared by dissolving 12.5 g potassium persulfate in deionized water in a 250-mL volumetric flask, and by diluting to calibrated volume with deionized water.

Stannous chloride, $SnCl_2 \cdot 2H_2O$, FW 225.63, "Baker Analyzed" ACS reagent grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

Stannous chloride, 15-percent, (w/v) solution: Prepared by dissolving 150 g stannous chloride in 300 mL concentrated hydrochloric acid and by diluting to 1 L with deionized water.

Copper nitrate, 1000 mg/L, cupric nitrate in dilute nitric acid, Fisher atomic absorption standard (Fisher Scientific Company, Fair Lawn, NJ) or equivalent.

Methyl mercuric chloride, CH_3HgCl, FW 251; Pfaltz and Bauer, Inc., Waterbury, CT, or equivalent.

STANDARDS

Mercury stock solution, 1000 mg/L, mercuric chloride in distilled water; Fisher atomic absorption standard (Fisher Scientific Company, Fair Lawn, NJ) or equivalent.

Mercury intermediate standard, 10 mg/L: Prepared by transferring 1.0 mL of 1000-mg/L stock solution to a 100-mL volumetric flask containing 90 mL deionized water and 1 mL concentrated nitric acid, and by diluting to calibrated volume with deionized water.

Mercury intermediate standards, 1 mg/L and 0.1 mg/L: Prepared by transferring 10.0 mL and 1.0 mL, respectively, of 10-mg/L intermediate standard to individual 100-mL volumetric flasks containing 90 mL deionized water and 1 mL concentrated nitric acid, and by diluting to calibrated volume with deionized water.

Methyl mercuric chloride stock solution, 900 mg/L Hg nominal concentration: Prepared by transferring 0.11-g CH_3HgCl into a 100-mL volumetric flask; the weighed aliquot was dissolved in deionized water and then diluted to calibrated volume with deionized water.

Methyl mercuric chloride intermediate standard, 9 mg/L Hg nominal concentration: Prepared by transferring 1.0-mL of the methyl mercuric chloride stock solution to a 100-mL volumetric flask containing 90 mL deionized water and 1 mL concentrated nitric acid, and by diluting to calibrated volume with deionized water.

Methyl mercuric chloride intermediate standards, 0.9 mg/L and 0.09 mg/L Hg nominal concentrations: Prepared by transferring 10.0 mL and 1.0 mL, respectively, of the nominal 9-mg/L intermediate standard to individual 100-mL volumetric flasks containing deionized water and 1 mL concentrated nitric acid, and by diluting to calibrated volume with deionized water.

ENVIRONMENTAL SAMPLES

NBS-SRM 1633a (Coal Fly Ash)

This Standard Reference Material (SRM), purchased from the National Bureau of Standards (NBS), Gaithersburg, MD, is a representative fly ash collected from coal-fired power plants; this fly ash material is generated from Pennsylvania and West Virginia coals. The certified concentration for mercury in NBS-SRM 1633a is 0.16 µg/g with an uncertainty of 0.01 µg/g. The estimated uncertainty is based on judgment and represents an evaluation of the combined effects of method imprecision, possible systematic errors among methods, and material variability for sample sizes of at least 250 mg.

The certified values for the principal matrix components include: silicon - 22.8 percent, iron - 9.40 percent, potassium - 1.88 percent, and calcium - 1.11 percent. Although not certified, a concentration value of 14 percent aluminum is provided for information use.

MESS-1 (Marine Sediment)

This reference material, purchased from the National Research Council of Canada (NRCC), Ottawa, Canada, is a freeze-dried sediment originally obtained from the Gulf of St. Lawrence (Miramichi River estuary). The reference value for mercury in MESS-1 is 0.171 µg/g with an uncertainty of 0.014 µg/g. The uncertainty represents 95-percent tolerance limits for an individual sub-sample of 500 mg or greater.

The principal matrix components and their reference concentrations include: silicon dioxide - 67.5 percent, aluminum oxide - 11.03 percent, iron(II) oxide - 4.36 percent, sodium oxide - 2.50 percent, potassium oxide - 2.24 percent, and magnesium oxide - 1.44 percent. The major and minor inorganic matrix components represent approximately 95 weight percent of the total sediment material.

Incinerator Fly Ash

A composite inorganic ash sample was prepared from incinerator ash obtained from four municipal refuse incinerator sites located in Florida, Massachusetts, New Jersey, and Oregon. The original composite sample was comprised of gray ash particles ranging in size from fine dust to approximately 2.5 cm in diameter. A representative sample of this bulk material was air-dried and pulverized with a clean rubber mallet. The large chunks of ash were removed by passing the sample through a 9.5-mm sieve. The remaining ash material was then consecutively passed through 40-mesh (420 micrometers) and 200-mesh (74 micrometer) sieves, placed in a plastic bag and homogenized by tumbling. Approximately 60 g of the sieved ash material were heated in a muffle furnace at a temperature of 600°C for approximately 24 hours to volatilize any endogenous mercury. No detectable mercury was measured in this treated composite ash sample, as characterized in Phase I by the amalgamation CV-AAS method.

Municipal Sewage Sludge

A composite sample of dried municipal sewage sludge was obtained from the Water Surveillance Laboratory of Columbus, Ohio. The sample was air-dried and then sieved to 100 mesh. The sieved material was homogenized by tumbling, and was then stored in a plastic sample bag. The mercury concentration of the composite sample, characterized in Phase I by the amalgamation CV-AAS method, was found to be approximately 1.4 µg/g.

Ground Water

A ground-water sample was obtained from a farm well west of Columbus, Ohio. The sample was filtered through 0.45-micron Millipore filter paper

and acidified to 1 percent (v/v) with nitric acid. The ground-water sample did not contain any detectable mercury, as characterized in Phase I by the amalgamation CV-AAS method.

Waste Water

A liquid waste sample was obtained from the Water Surveillance Laboratory of Columbus, Ohio. The waste water sample did not contain any detectable mercury.[4]

Deionized Water

Laboratory deionized water was used as the aqueous sample in Phase II. Laboratory deionized water acidified to one percent with nitric acid was used in Phase III. The deionized water samples did not contain any detectable mercury.

SECTION 5

EXPERIMENTAL PROCEDURES

The environmental samples were prepared for analysis by using the digestion procedures described in revised SW-846 Methods 7470 and 7471 which are included as Appendices A and B. All sample digests were diluted to volume in 100-mL volumetric flasks with deionized water following the addition of the sodium chloride-hydroxylamine hydrochloride reagent solution to reduce manganese dioxide and excess permanganate to the soluble divalent manganese form. This procedure permitted sampling of multiple aliquots and further dilutions as needed. The sample aliquot added to the reduction-aeration vessel was diluted to 100 mL with Type II water.

All mercury concentrations were calculated by the use of 4-point calibration curves. The four points were comprised of a reagent blank and three mercury standards within the linear range of the amalgamation CV-AAS method. In most cases, the calibration standards contained 10, 50, and 100 ng of mercury, respectively.

The mercury concentration data submitted to Battelle for each analysis option and for each sample type in Phase III were statistically analyzed. The accuracies of the revised Methods 7470 and 7471 were assessed by comparing the measured mercury concentrations reported by the laboratories with the target mercury concentrations for each sample. The precisions of the methods were estimated for each sample in Options A and B from the standard deviations calculated for duplicate and triplicate analyses, respectively. The ruggedness of the methods was qualitatively derived from the relative accuracies and precisions.

SECTION 6

RESULTS AND DISCUSSION

PHASE I - LABORATORY TESTING OF THE SILVER-WOOL AMALGAMATION CELLS AND CHARACTERIZATION OF THE INTERLABORATORY STUDY SAMPLES

Testing of Amalgamation Cells

To facilitate interpretation of the data from the participating laboratories, the variability in instrument response for different silver-wool amalgamation cells was characterized. To minimize variability in the instrument responses, the silver-wool amalgamation cell must possess the following two characteristics: (1) quantitative amalgamation of at least 100 ng of mercury, and (2) a uniform rate of thermal desorption of amalgamated mercury. The second characteristic is particularly important for the present method because mercury is quantified by peak-height measurement. Differences in desorption rates among amalgamation cells could lead to different absorbance peak heights, thus adversely affecting sensitivity. If peak-area integration is used for quantification, a uniform rate of thermal desorption may be less important.

The uniformity of performance for the 23 silver-wool amalgamation cells was verified before the cells were distributed to the participating laboratories. The parameter used to assess uniformity of performance among the amalgamation cells was the slope of their calibration curves. If the amalgamation cells provide uniform performance in terms of amalgamation efficiency and thermal-desorption rates, the slopes and intercepts of the calibration curves obtained for the respective amalgamation cells should be similar.

Each amalgamation cell to be tested was positioned within the instrument configuration; the inlet was connected to the cold-vapor apparatus but the outlet was disconnected from the absorption cell. With nitrogen purge gas flowing through the apparatus, the Variac autotransformer set to 20 volts output was turned on, and each amalgamation cell was pre-conditioned by heating for 2.5 minutes to clean the silver-wool plug before conducting the sensitivity check.

Four-point calibration curves were constructed for each of the first 8 amalgamation cells using a reagent blank and aqueous standards containing 10, 50, and 100 ng of mercury. The average value of the slope of the calibration curve obtained for these cells was 0.0058 absorbance units/ng of mercury. The standard deviation of these measurements was 0.0006 absorbance units/ng, which yields a relative standard deviation of 10 percent. The slopes of the calibration curves for the 8 amalgamation cells ranged from 0.0048 to 0.0065 absorbance units/ng of mercury, and the intercepts ranged from -0.003 to 0.006 absorbance units. The average intercept, 0.002 absorbance unit, is small and sufficiently close to zero.

The relative sensitivities of the remaining 15 amalgamation cells were verified in a more expeditious manner. After calibrating the instrument with a single 4-point curve by using the aqueous mercury standards described above, the performance of each of these amalgamation cells was checked with a single 50-ng Hg standard. The calibration curve used to assess the cell performances had a slope of 0.0052 abs/ng of mercury and an intercept of 0.003 absorbance unit; the slope and intercept were within the experimental ranges of those values determined for the first 8 cells. The average recovery of the 50-ng Hg standard for each of these 15 cells was 98 percent, with an experimental uncertainty of 6 percent. The range of recoveries was 89 to 108 percent. These results indicate that the instrument responses for 50 ng Hg for the 15 amalgamation cells are within $\pm$ 10 percent of the target concentration which, based on Battelle's experience, constitutes a satisfactory performance.

The overall testing results indicate uniformity in performance among the 23 amalgamation cells with respect to amalgamation efficiency and thermal-desorption characteristics. The differences in instrument responses for the different amalgamation cells are expected to be small compared to the overall measurement variabilities between the participating laboratories.

Characterization of Interlaboratory Study Samples

The aqueous and solid environmental samples to be used in the interlaboratory study were characterized for endogenous mercury content by using the revised Methods 7470 and 7471 presented in Appendices A and B, respectively. Replicate 0.2-g portions of solid samples and 20-mL or 50-mL portions of liquid samples were used for the analyses.

NBS-SRM 1633a (Coal Fly Ash)--

NBS-SRM 1633a (Coal Fly Ash) was selected as a representative solid waste sample to be used in a preliminary evaluation of the revised Method 7471 in Phase II. This sample was selected because it had a certified mercury value in the concentration range useful for evaluating the silver-wool amalgamation CV-AAS method, and the homogenous material would not introduce errors due to sample heterogeneity.

The coal fly ash sample was analyzed by Battelle staff according to the revised Method 7471. The mercury results for analyses of duplicate 0.2-g portions were 0.145 µg/g and 0.160 µg/g. These results are in agreement with the certified mercury concentration of 0.16 µg/g. The recoveries of inorganic mercury predigestion spikes added to the fly ash samples were 130 percent and 130 percent for duplicate 10-ng mercury spikes, and 112 percent and 104 percent for duplicate 50-ng mercury spikes.

Incinerator Ash--

A composite sample of municipal refuse incinerator ash was used as one of the solid waste samples for the evaluation of the revised Method 7471 in Phase III. The incinerator ash sample was analyzed by Battelle staff according to the revised Method 7471 to determine the endogenous mercury

content that would be used as the target mercury concentration for the participating laboratories. No detectable mercury was found in triplicate 0.2-g portions of the composite ash sample. No inorganic or organic mercury predigestion spiking studies were performed.

Municipal Sewage Sludge--

A municipal sewage sludge was one of the solid waste samples used for the evaluation of the revised Method 7471 in Phase III. Replicate portions of the sludge sample were analyzed on different days by Battelle staff according to the revised Method 7471 to determine the endogenous mercury content that would be used as the target mercury concentration for the participating laboratories. The average mercury concentration determined in 8 replicate 0.2-g portions of the sewage sludge sample was 1.4 µg/g; the compiled results ranged from approximately 1.2 µg/g to 1.4 µg/g of mercury. This average mercury value agrees with data previously obtained from analyses conducted by the Columbus Water Surveillance Laboratory.[4] The results indicate that the mercury content of the municipal sewage sludge is homogeneous to approximately ± 0.1 mg/kg. Of these 8 replicate measurements, some of the portions were analyzed by using inorganic mercury standards for calibration while the other portions were analyzed by using organic mercury calibration standards. The average recoveries of duplicate 90-ng and 180-ng Hg predigestion spikes (as methyl mercuric chloride) were 75 percent and 90 percent, respectively, and the average recoveries of duplicate 100-ng and 200-ng Hg predigestion spikes (as inorganic mercuric chloride) were 108 percent and 106 percent, respectively. The overall recoveries of organic and inorganic mercury added as predigestion spikes are within ± 25 percent of full recovery.

Ground Water--

A ground-water sample was used as one of the aqueous environmental samples for the evaluation of the revised Method 7470 in Phase III. The ground-water sample was analyzed by Battelle staff according to the revised Method 7470 to determine the endogenous mercury content that would be used as the target mercury concentration for the participating laboratories. No detectable mercury was found in four replicate 50-mL portions of the ground-water sample. The average inorganic spike recoveries of four sample replicates were 106 percent for 50-ng mercury spikes and 105 percent for 100-ng mercury spikes.

Waste Water--

A waste-water sample was one of the aqueous samples used for the evaluation of the revised Method 7470 in Phase III. Although not analyzed at Battelle, the waste-water sample did not contain any detectable endogenous mercury based on the results of analyses conducted by the Water Surveillance Laboratory of Columbus, Ohio.[4]

PHASE II - PRELIMINARY EVALUATION OF THE TECHNICAL CAPABILITIES OF THE PARTICIPATING LABORATORIES

Selection of the Laboratories

The initial goal of Phase II was to identify laboratories that would want to become acquainted with the silver-wool amalgamation accessory and the experimental procedures for successfully implementing the CV-AAS method for trace mercury determinations in environmental and waste samples. Requests for proposals to participate in the interlaboratory study were sent to 90 laboratories; copies of the revised Methods 7470 and 7471 were also enclosed to provide the laboratories a detailed technical description of the silver-wool amalgamation step. Twenty-two laboratories responded with proposals which included equipment descriptions, qualifications of personnel, previous relevant experience, and cost bids. Contracts to participate in Phase II were sent to the 22 laboratories. Eighteen laboratories responded with signed contracts. A package containing the necessary materials was shipped to each of these 18 laboratories that had signed contracts, and to one additional laboratory that participated at no cost. Each package contained: (1) a tested silver-wool amalgamation cell, (2) instructions for the installation and use of the amalgamation cell, (3) two samples and appropriate standard solutions, (4) instructions for the preparation and analysis of the samples, and (5) instructions for reporting the analytical results to Battelle. One laboratory with a signed contract withdrew at the beginning of Phase II after receiving the package, leaving a total of 18 participating laboratories. Throughout this report, these laboratories are identified by numbers.

Samples and Instructions for Analysis

The two samples shipped to the participating laboratories consisted of deionized water for the evaluation of revised Method 7470 and NBS-SRM 1633a (Coal Fly Ash) for the evaluation of revised Method 7471. A spiking solution, containing mercury at a concentration of 1.5 mg/L, was included for spiking the deionized water. The participants were instructed to add 50 µL of the 1.5-mg/L spiking solution (equivalent to 75 ng Hg) to a 20-mL aliquot of the water sample as a predigestion spike. The laboratories were also provided a stock solution containing mercury at a concentration of 1000 mg/L to be used for preparing intermediate and final calibration standards.

For the analyses of the samples, the participants were instructed to: (1) construct a 4-point calibration curve comprised of the absorbances for a reagent blank, 10-ng, 50-ng, and 100-ng Hg standards, (2) analyze the spiked water sample according to the revised Method 7470, (3) analyze the coal fly ash sample according to the revised Method 7471, and (4) prepare and analyze one reagent blank each for the revised Methods 7470 and 7471. For the reporting of the analytical results, the participants were instructed to: (1) report the slopes of the calibration curves for both methods in units of absorbance/nanogram of mercury, (2) report the measured concentration of mercury in the spiked water sample in units of mg/L, (3) report the measured concentration of mercury in the coal fly ash sample in units of mg/kg, and (4) report the absorbance values for the reagent blanks for both methods.

Laboratory Results

The slopes of the calibration curves and the mercury absorbance values for the reagent blanks obtained from the 18 laboratories are summarized in Table E-1 of Appendix E. These data were not statistically examined for outliers or as criteria for selecting specific laboratories to participate in Phase III. Five laboratories were unable to report data for at least one of the revised methods because of analytical and/or instrumental difficulties.

The slopes of the calibration curves for the two revised methods ranged from 0.0001 to 0.0056 absorbance units/nanogram. Ten of the 18 laboratories reported slopes between 0.003 and 0.006 absorbance units/nanogram for at least one of the revised methods. Battelle researchers have found that this is a typical range for the slope of the calibration curve obtained by using the amalgamation CV-AAS system according to the specific instructions described in revised Methods 7470 and 7471.

The mercury absorbance values for the reagent blanks ranged from 0.001 to 0.644 absorbance units. Ten laboratories reported reagent blank values less than 0.03 absorbance unit. Battelle researchers have consistently measured absorbance values between 0.02 and 0.03 absorbance units for reagent blanks analyzed according to the revised Methods 7470 and 7471. Based on a typical instrument calibration slope of 0.005 absorbance units/nanogram, reagent blank absorbances in this range correspond to approximately 5 ng Hg. Reagent blanks for aqueous mercury calibration standards, consisting only of the stannous chloride reductant and deionized water, generally produce 0.001 absorbance unit; this is negligible relative to the absorbance values for the reagent blanks carried through the digestions. Some of the apparent low reagent blank values reported by the laboratories may be suppressed in those cases in which the reported calibration slopes were lower than the typical range of values.

The results for the measured mercury concentrations in the spiked water sample and the coal fly ash sample are summarized in Table 1. The target mercury values are 0.00375 mg/L for the spiked water sample and 0.16 mg/kg for the coal fly ash sample. For the specified sample sizes, these values correspond to absolute mercury target values of 75 ng for the spiked water sample and 32 ng for the coal fly ash sample that should be measured by the instrument; both of these mercury values fall within the optimal measurement range of the amalgamation CV-AAS method.

As shown in Table 1, two laboratories did not submit mercury concentration results for the spiked deionized water sample, and five laboratories did not submit mercury concentration results for the coal fly ash sample. These laboratories experienced analytical and/or instrumental problems with these preliminary sample analyses. For those laboratories that reported results, the measured mercury concentrations for the spiked water sample ranged from 0.00076 to 0.076 mg/L, and for the coal fly ash sample from 0.04 to 48 mg/kg.

TABLE 1. SUMMARY OF MERCURY CONCENTRATIONS IN DEIONIZED WATER SPIKED WITH INORGANIC MERCURY AND IN COAL FLY ASH

Laboratory Identification Number	Method 7470 (Water Sample) Mercury Concentration[a] (mg/L)	Method 7471 (Coal Fly Ash Sample) Mercury Concentration[b] (mg/kg)
949	0.0041	- - -
950	0.00076	0.22
951	- - - -	- - -
952	0.0030	0.14
953	0.0030	0.14
954	0.0074	0.40
955	0.0046	0.71
956	0.0023	0.04
957	- - - -	- - -
958	0.0034	- - -
959	0.00091	0.41
960	0.0016	0.68
961	0.0054	- - -
962	0.0046	0.23
963	0.076	48
964	0.0074	1.1
965	0.0035	0.15
966	0.0036	0.17

[a] Target mercury concentration = 0.00375 mg/L.

[b] NBS-SRM 1633a; certified mercury concentration = 0.16 ± 0.01 mg/kg.

The percent recoveries of the target mercury concentrations in the spiked water sample and the coal fly ash sample are summarized in Table 2. The percent recovery is calculated as 100 times the measured concentration divided by the target concentration. Excluding the results from Laboratory No. 963 for spiked deionized water, the mercury recoveries ranged from 20 percent (a 5-fold negative bias) to 200 percent (a 2-fold positive bias) for all laboratories as well as for just the Phase-III laboratories. Excluding also the results from Laboratory No. 963 for the coal fly ash, the mercury recoveries ranged from 25 percent (a 4-fold negative bias) to 690 percent (a 7-fold positive bias) for all laboratories, and from 88 to 690 percent for the Phase III-laboratories.

A summary of the statistics across all laboratories for the mercury measurements on the spiked deionized water and coal fly ash samples is presented in Table 3. The means and standard deviations, reported as percent recoveries, were calculated for all laboratories and also for only those eventually selected for Phase III. In Table 3 and in all subsequent tables containing statistical data, the means and standard deviations are reported to two significant figures.[5] The results from Laboratory No. 963 were excluded as outliers from the statistical treatment. After these data values were removed, the remaining data were smoothly dispersed, and no additional outliers were obvious.

Although the measured mercury concentrations from Laboratory No. 963 are in appreciable error, the reported slopes of their calibration curves are within the expected range. However, very high reagent blank values were reported. High reagent blank values consistent with the positive biases obtained for the sample analyses indicate that reagent contamination, and possibly sample contamination, were out of control. Although not verified, inaccurate calculations by the laboratory staff may also have contributed to the magnitude of the erroneous data submitted to Battelle.

As shown in Table 3, the grand mean of mercury recovery for the spiked water sample was 99 percent for all laboratories and 110 percent for the Phase-III laboratories. The standard deviations of the percent mercury recoveries were 53 percent and 57 percent, respectively. The grand means for the spiked water sample correspond to nearly complete recoveries of the target mercury concentration by using the revised Method 7470. The grand mean of mercury recovery for the coal fly ash sample was 230 percent for all laboratories as well as for just the Phase-III laboratories; the standard deviations of the mercury recoveries were 200 percent and 210 percent, respectively. The grand means for the coal fly ash sample correspond approximately to a 2-fold positive bias by using the revised Method 7471; moreover, the recovery data are considerably more dispersed than the recovery data for the spiked water sample. This may be due to the lower mercury concentration measured at the instrument for the fly ash sample, and to weighing errors and other uncertainties when manipulating solid samples in preparation for analysis. In general, the high dispersion of data between laboratories for both samples indicates a lack of ruggedness for the amalgamation CV-AAS method in this testing phase of the study.

TABLE 2. SUMMARY OF PERCENT RECOVERIES OF TARGET MERCURY CONCENTRATIONS IN SPIKED DEIONIZED WATER AND COAL FLY ASH

Laboratory Identification Number	Percent Recovery	
	Spiked Deionized Water	Coal Fly Ash
949	110	- - -
950[a]	20	140
951	---	---
952[a]	80	88
953[a]	80	88
954[a]	200	250
955[a]	120	440
956	61	25
957[a]	---	---
958	91	---
959	24	260
960	43	420
961	140	---
962[a]	120	140
963	2030[b]	30000[b]
964[a]	200	690
965[a]	93	94
966[a]	96	110

[a] Laboratories selected for Phase III.

[b] Recoveries for Laboratory Number 963 were not used when calculating means and standard deviations.

TABLE 3. STATISTICAL SUMMARY OF MERCURY MEASUREMENTS ON SPIKED DEIONIZED WATER AND COAL FLY ASH

Number of Laboratories	Percent Recoveries	
	Spiked Deionized Water	Coal Fly Ash
All Labs[a]		
Mean	99	230
Standard Deviation	53	200
Phase III Labs		
Mean	110	230
Standard Deviation	57	210

[a] Recoveries for Laboratory Number 963 were not used when calculating means and standard deviations.

The data reported by some of the participating laboratories for these preliminary sample analyses are in appreciable error. Possible contributing factors to the wide range of results, especially for the coal fly ash sample, include high absorbance values for the reagent blanks resulting from sample digestions, a propagation of errors in the calculated data submitted to Battelle, and the general lack of operator experience with the silver-wool amalgamation technique. Some laboratories measured reagent blank values as high as 0.6 absorbance unit, which is equivalent to approximately 120 ng of mercury based on a calibration slope of 0.005 absorbance unit/ng; such a reagent blank value exceeds the linear range of the amalgamation CV-AAS method. Battelle staff discussed the results with many of the laboratories; recommendations for improvements in controlling mercury contamination of the reagent blank and test sample, as well as suggestions for implementation of the amalgamation CV-AAS system, were provided.

The results of the preliminary sample analyses in Phase II were used as a qualitative guideline but not as absolute criteria for the selection of laboratories for participation in Phase III. Five laboratories obtained results which were in close agreement with the target mercury values for both samples. Five other laboratories obtained less satisfactory results but exhibited sufficient interest and enthusiasm in the silver-wool amalgamation technique; these 5 laboratories were judged to be capable participants in Phase III. The remaining 8 laboratories did not exhibit

sufficient technical proficiency or enthusiastic interest to be invited to participate in Phase III.

PHASE III - INTERLABORATORY EVALUATION OF THE SILVER-WOOL AMALGAMATION CV-AAS METHOD

Ten of the 18 participating laboratories in Phase II were invited to participate in the interlaboratory study in Phase III. These 10 laboratories, listed alphabetically in Table 4, are identified in the subsequent tables from Phase III by numbers which are not correlated with the alphabetical listing in Table 4.

TABLE 4. SUMMARY OF LABORATORIES PARTICIPATING IN PHASE III

Laboratory
Alliance Technologies Corporation (Bedford, MA)
Anatech Laboratories, Inc. (Santa Rosa, CA)
Conoco, Inc. (Ponca City, OK)
Environmental Monitoring & Services, Inc. (Camarillo, CA)
Harris Laboratories, Inc. (Lincoln, NE)
Northern Laboratories and Engineering, Inc. (Valparaiso, IN)
Pittsburgh Applied Research Corporation (Pittsburgh, PA)
Raba-Kistner Consultants, Inc. (San Antonio, TX)
Radian Corporation (Sacramento, CA)
University of Iowa Hygienic Laboratory (Iowa City, IA)

The Phase III study consisted of two options which differed in the number of samples to be analyzed; Option A was comprised of 16 samples and Option B was comprised of 24 samples. Five of the 10 laboratories were selected for each option. The designations of the laboratories for the specified options were based on their previous results in Phase II as well as on budgetary constraints.

Interlaboratory Study Samples

Two different sample sets comprised of three solid and three aqueous samples were shipped to the participants in Phase III. Some of the samples required additions of a predigestion spike. The sample sets, denoted as Option A and Option B, are listed in Appendices C and D, respectively. Options A and B differed principally in the number of replicate samples designated for each sample type; Option A samples were supplied in duplicate and Option B samples were supplied in triplicate. The samples were shipped unspiked to avoid potential losses of trace mercury spikes added to samples with a reducing matrix. Predigestion spiking solutions containing organic and inorganic mercury were sent to the participants with spiking instructions. One solid sample in Option B was also to be spiked with copper, a potential interferent in CV-AAS analyses for mercury.

Instructions for Analysis and Reporting

In addition to the study samples and the appropriate spiking solutions, the participating laboratories were provided a coded sample list and a set of instructions for their designated option. The instructions included a list comprised of the coded samples, the amount of sample to use, and the kind and volume of predigestion spiking solution to add. The spiking solutions were labeled to indicate for which sample they were to be used. For the reporting of the analytical results, the participants were instructed to: (1) report the slopes of the calibration curves for samples analyzed by the revised Methods 7470 and 7471, both in units of absorbance units/nanogram of mercury, (2) report all sample analysis data both in units of absorbance and total nanograms of mercury, and (3) report the data for the reagent blanks for the revised Methods 7470 and 7471 both in units of absorbance and total nanograms of mercury.

Laboratory Results - Calibration Data

The slopes of the calibration curves and the mercury absorbance values for the reagent blanks obtained by the 10 laboratories are summarized in Table E-2 of Appendix E. The slopes of the calibration curves ranged from 0.0010 to 0.0065 absorbance units/nanogram of mercury. Six of the 10 laboratories reported slopes within the range experienced by Battelle staff (0.003 and 0.006 absorbance units/nanogram). The absorbance values for the reagent blanks ranged from -0.004 to 0.075 absorbance units. Eight of the 10 laboratories reported reagent blank values less than 0.03 absorbance unit. Based on a typical calibration slope of 0.005 absorbance unit/nanogram, a reagent blank value of 0.03 absorbance unit corresponds to a maximum concentration of 6 ng Hg in the reagent blank.

In general, the 10 laboratories in Phase III reported a lower dispersion and a narrower range of results for calibration and reagent blank data than the 18 laboratories in Phase II. The 10 Phase-III laboratories represent a more consistent range of personnel skills and demonstrated competence in trace analysis. The lower dispersion in the data may also be

a direct result of the acquired experience and familiarity with the silver-wool amalgamation technique by the 10 laboratories from their participation in the Phase II study.

Laboratory Results - Sample Analyses

The results of the sample analyses by the 10 laboratories are compiled by sample type for the revised Methods 7470 and 7471. The measured concentrations for the individual replicates and statistical information (mean and standard deviation) are provided for each laboratory and for each sample type. In an attempt to characterize the interlaboratory accuracy and precision of the amalgamation CV-AAS methods, a statistical summary of the mercury concentration data for each analysis option and for each sample type has also been compiled. The statistical summaries of the interlaboratory data for the revised Methods 7470 and 7471 are presented in Tables 5 and 6, respectively. In all statistical analyses, the means and standard deviations are reported in concentration units for those environmental samples originally having nondetectable endogenous mercury concentrations, and in percent recoveries for those samples having detectable target mercury concentrations. The percent recoveries are calculated as 100 times the measured concentration divided by the target concentration.

Outlier tests were performed on the laboratory means for each option within each sample type by using the maximum normed residual test.[6] Laboratory No. 964 was identified as an outlier for the following sample types: marine sediment MESS-1, incinerator fly ash, ground water, waste water spiked with inorganic mercury, and dilute nitric acid spiked with inorganic mercury. In addition, Laboratory No. 966 was found to be an outlier for ground water, as was Laboratory No. 952 for waste water spiked with inorganic mercury. Because the concentration data reported by Laboratory No. 964 in Option A are statistical outliers in the majority of the sample types, these data have been uniformly excluded from statistical treatment for all sample types.

An explanation of the statistical terms in Tables 5 and 6 is provided below. The average mercury concentration or percent recovery over all laboratories in a given option is reported in the third column. The fourth column contains the pooled within-laboratory standard deviations of the mercury concentrations or percent recoveries. The within-laboratory variances are simply calculated as the averages of the variances for the individual laboratories. The between-laboratory standard deviations of the mercury concentrations or percent recoveries are reported in the fifth column. This statistic characterizes the variabilities in the true average mercury concentration or percent recovery values across the laboratories. The between-laboratory variances are calculated according to the following formula:

$$S_B^2 = \frac{1}{n} \left(S_{\bar{x}}^2 - S_w^2 \right)$$

where $S_{\bar{x}}^2$ is the variance of the average percent recoveries for an individual laboratory, n is the number of sample results used to calculate the average

TABLE 5. STATISTICAL SUMMARY OF MERCURY MEASUREMENTS[a] USING REVISED METHOD 7470

Sample	Option	Mean	Pooled Std. Dev.	Between Std. Dev.	Total Std. Dev.
Samples Having Nondetectable Target Concentrations[b]					
Ground Water	A	4	1.8	1.4	2.3
Ground Water[c]	B	6	1.5	2.1	2.6
Samples Having Detectable Target Concentrations[d]					
Waste Water, Spiked	A	140	17	45	48
Waste Water,[e] Spiked	B	150	15	39	42
Dilute Nitric Acid, Spiked	A	82	27	27	38
Dilute Nitric Acid, Spiked	B	82	31	17	36

[a] Results for Laboratory Number 964 in Option A were not used in the statistical analyses for any sample.

[b] Results are in absolute concentration units (ng).

[c] Results for Laboratory Number 966 were not used in the statistical analyses for this sample.

[d] Results are percent recovery.

[e] Results for Laboratory Number 952 were not used in the statistical analyses for this sample.

TABLE 6. STATISTICAL SUMMARY OF MERCURY MEASUREMENTS[a] USING REVISED METHOD 7471

Sample	Option	Mean	Pooled Std. Dev.	Between Std. Dev.	Total Std. Dev.
Samples Having Nondetectable Target Concentrations[b]					
Incinerator Fly Ash	A	0.021	0.0090	0.0076	0.012
Incinerator Fly Ash	B	0.074	0.021	0.041	0.046
Samples Having Detectable Target Concentrations[c]					
Marine Sediment MESS-1	A	110	6.5	10	12
Marine Sediment MESS-1	B	110	48	0	48
Incinerator Fly Ash, Spiked	A	74	8.6	32	34
Incinerator Fly Ash, Spiked	B	39	15	11	19
Municipal Sewage Sludge	A	90	14	18	22
Municipal Sewage Sludge	B	88	20	21	30
Municipal Sewage Sludge, Spiked	A	97	26	25	36
Municipal Sewage Sludge, Spiked	B	90	12	26	28

[a] Results for Laboratory Number 964 in Option A were not used in the statistical analyses for any sample.

[b] Results are in relative concentration units (mg/kg).

[c] Results are in percent recovery.

percent recovery, for each laboratory, and S_w^2 is the within-laboratory variance. If $S_{\bar{x}}^2$ is less than S_w^2, then S_B^2 is set to zero. The total standard deviations are reported in the last column. The total variance is simply the sum of the within-laboratory and between-laboratory variances.

Revised Method 7470--

Ground Water--The results for the measured concentrations reported by the individual laboratories are summarized in Table E-3 of Appendix E. In addition to the data from Laboratory No. 964 in Option A, the data from Laboratory No. 966 in Option B have been excluded as outliers for the statistical analyses. The grand means for both options in Table 5 are less than 10 ng Hg which is expected for a water sample originally having a nondetectable target mercury concentration. Absolute mercury concentrations less than 10 ng are definitively imprecise and are very close to the baseline noise level of the amalgamation CV-AAS method. Even taking into account the spreads indicated by the total standard deviations for the two options, the grand means did not exceed 10 ng Hg.

Spiked Waste Water--This sample was to have been spiked with inorganic mercury to provide target mercury concentrations of 50 ng for Option A and 25 ng for Option B. The results for the measured mercury concentrations reported by the individual laboratories are summarized in Table E-4 of Appendix E. In addition to the data from Laboratory No. 964 in Option A, the data from Laboratory No. 952 in Option B have been excluded as outliers for the statistical analyses. The mean percent recoveries for the 8 laboratories ranged from 88 to 220 percent in Option A and from 89 to 240 percent in Option B. The standard deviations ranged from 6 to 21 percent in Option A and from 0 to 28 percent in Option B. As shown in Table 5, the grand mean recoveries for both analysis options are not within 15 percent of full recovery of the spiked mercury concentrations. These results represent a potential positive bias of 40 to 50 percent for this sample.

Spiked Dilute Nitric Acid--This sample was to have been spiked with inorganic mercury to provide a target mercury concentration of 25 ng for Options A and B. The results for the measured mercury concentrations reported by the individual laboratories are summarized in Table E-5 of Appendix E. The mean percent recoveries ranged from 18 to 130 percent in Option A and from 9 to 120 percent in Option B. The standard deviations ranged from 0 to 40 percent in Option A and from 2 to 47 percent in Option B. As shown in Table 5, the grand mean recoveries for both analysis options are not within 15 percent of the spiked mercury concentration by only narrow margins. These results represent a potential negative bias for this sample.

Revised Method 7471--

Marine Sediment MESS-1--The results reported by the individual laboratories for the measured mercury concentrations in the marine reference sediment are summarized in Table E-6 of Appendix E. The mean percent recoveries ranged from 100 to 140 percent for Option A and from 66 to 150 percent for Option B. The standard deviations ranged from 4 to 8 percent for Option A and from 3 to 97 percent for Option B. As shown in Table 6, the grand mean recoveries for both analysis options in Table 6 are within 15 percent of full recovery of the target mercury concentration.

Incinerator Fly Ash--The results reported by the individual laboratories for the measured mercury concentrations in the incinerator fly ash are summarized in Table E-7 of Appendix E. The mean concentrations ranged from <0.005 to 0.038 mg/kg for Option A and from 0.019 to 0.20 mg/kg for Option B. Most laboratories reported measurable mercury concentrations although the sample contained no detectable mercury when it was packaged and shipped to the laboratories. These data suggest that the sample became contaminated, measurement inaccuracies were introduced from uncompensated reagent blank absorbances, or some other unidentified measurement bias existed for the laboratory's instrument configuration. Based on a quantification limit of 10 ng and on a sample weight of 0.2 g, mercury concentrations less than 0.05 mg/kg were expected for such a solid sample not having a detectable mercury concentration. As shown in Table 6, the grand mean for Option A is less than 0.05 mg/kg. However, the grand mean for Option B is greater than 0.05 mg/kg which indicates a possible positive bias.

Spiked Incinerator Fly Ash--This sample was to have been spiked with inorganic mercury for both options and with copper for Option B. The results reported by the individual laboratories for the measured mercury concentrations in the spiked incinerator fly ash are summarized in Table E-8 of Appendix E. The mean percent recoveries ranged from 8 to 120 percent for Option A and from 13 to 72 percent for Option B. With the exception of Laboratory No. 957, the percent recoveries for the laboratories in both options were low by as much as ten fold. With the exception of Laboratory No. 966, the standard deviations for within-laboratory analyses in both options were less than 11 percent. As shown in Table 6, the grand mean recovery for Option A analyses in Table 6 is within approximately 25 percent of full recovery of the spiked mercury concentration. However, the grand mean recovery for Option B analyses is low by more than two fold.

The low recoveries of spiked inorganic mercury in Option B suggest that 1 mg copper, in general, interferes with the amalgamation CV-AAS analyses. The results of this interlaboratory study contradict the results of the single-laboratory study which revealed that copper concentrations as high as 1 mg per 0.2-g test portion of NBS-SRM 1646 (Estuarine Sediment) did not interfere with the recovery of the certified mercury concentration.[2,3] Such inconsistency between the single-laboratory and the interlaboratory results for the copper interference test indicates a relative lack of ruggedness of the revised Method 7471.

Municipal Sewage Sludge--The results reported by the individual laboratories for the measured mercury concentrations in the municipal sewage sludge are summarized in Table E-9 of Appendix E. The mean percent recoveries ranged from 61 to 130 percent for Option A and from 13 to 110 percent for Option B. With the exception of Laboratory No. 953, the mean concentrations for the laboratories in Option B were within 10 percent of the target mercury concentration. The standard deviations ranged from 0.5 to 27 percent in Option A and from 5 to 32 percent in Option B. As shown in Table 6, the grand mean recoveries for both Option A and Option B are within 15 percent of full recovery of the target mercury concentration.

Spiked Municipal Sewage Sludge--This sample was to have been spiked with mercury as methyl mercuric chloride to investigate the recoveries of organic mercury. The results reported by the individual laboratories for the measured mercury concentrations in the spiked municipal sewage sludge are summarized in Table E-10 of Appendix E. The mean percent recoveries ranged from 54 to 160 percent in Option A and from 12 to 130 percent in Option B. The standard deviations ranged from 2 to 48 percent in Option A and from 3 to 25 percent in Option B. As shown in Table 6, the grand mean recoveries for both analysis options are within 15 percent of full recovery of the target mercury concentrations.

Summary of the Interlaboratory Results

The high dispersion of the interlaboratory data precludes any statistical treatment of the results for the revised Methods 7470 and 7471 that is more rigorous than the analyses conducted and summarized in Tables 5 and 6, respectively. As shown in Table 5 for the revised Method 7470, the total standard deviations for Options A and B are similar for each of the 3 test samples. However, as shown in Table 6 for the revised Method 7471, neither option demonstrates a consistently lower total standard deviation for all samples. For example, the total standard deviations of the results in Option A are 4-fold lower than those in Option B for the incinerator fly ash and the marine reference sediment samples. However, the total standard deviation in Option B is approximately 2-fold lower than that in Option A for the spiked incinerator fly ash sample. The total standard deviations of the results in both options are similar for the unspiked and the spiked municipal sewage sludge sample. The relative differences between the total standard deviations in Options A and B by the revised Method 7471 for the 5 samples appear to be random.

With the exception of the spiked waste-water sample in Table 5 and of the spiked incinerator fly-ash sample in Table 6, the grand means using the revised Methods 7470 and 7471, respectively, are generally within 25 percent of the target values. However, the total standard deviations for all sample types represent relative standard deviations as high as 50 percent. Because of such highly dispersed results, in addition to the contradictory results of the copper interference test, the revised Methods 7470 and 7471 presently lack the necessary ruggedness to be successfully used for routine testing by analytical laboratories without additional analyst training and demonstration of proficiency.

REFERENCES

1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 2nd Edition, July 1982, U. S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

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APPENDIX A

METHOD 7470 (Proposed Revision)

MERCURY (MANUAL AMALGAMATION COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure recommended for determining low concentrations of mercury in mobility procedure extracts, aqueous wastes, and groundwaters. All samples must be subjected to an appropriate digestion step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the samples must be prepared according to the procedure discussed in this method.

2.2 This method, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state, aerated from solution by a nitrogen purge, and concentrated by amalgamation on silver wool. The amalgamated mercury is thermally volatilized from the silver wool by resistance heating of a nichrome wire wrapped around Pyrex tubing containing the silver wool and is then carried by the nitrogen purge gas into the glass absorption cell for the atomic absorption measurement. The analytical calibration curve is based on the maximum absorbance (peak height) determined for each measurement.

2.3 The typical instrument detection limit for this method is approximately 1 ng (0.02 µg/L for a 50-mL sample aliquot).

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. In a single-laboratory study, concentrations as high as 2 mg of sulfide as sodium sulfide per sample aliquot did not interfere with the recovery of inorganic mercury from a simulated aqueous waste.

3.2 Copper has been reported to interfere; however, in a single-laboratory study, copper concentrations as high as 1 mg per sample aliquot had no significant effect on the recovery of inorganic mercury from a simulated aqueous waste.

3.3 High levels of chloride in seawaters, brines, and industrial effluents have been reported to interfere; however, in a single-laboratory study, concentrations as high as 3.4 g sodium chloride per sample aliquot did not interfere with the recovery of inorganic mercury from a simulated aqueous waste. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the absorption cell. This may be accomplished by using an excess of hydroxylamine sulfate or hydroxylamine hydrochloride reagent (25 mL). In addition, the dead air space in the

reduction-aeration sample cell must be purged before adding stannous sulfate or stannous chloride. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this digestion method in previous studies.

3.4 Certain volatile organic materials may absorb at the 253.7 nm wavelength; however, no nonspecific absorption interferences were observed for a simulated aqueous waste spiked with benzene and methyl ethyl ketone.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit having an open sample atomization area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the spectrophotometric measurement of mercury by using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange, variable-speed recorder with a one-second time constant that is compatible with the photometric detection system is suitable.

4.4 Absorption cell: A cylindrical glass cell having entrance and exit ports on the side and quartz end-windows to transmit ultraviolet radiation is suitable. A cylindrical cell, 1 inch in diameter (o.d.) and 6 inches in length, has been found to be an appropriate geometry. The absorption cell is strapped to a burner head assembly for convenient positioning and for two-dimensional alignment in the optical path of the sample atomization area of the atomic absorption spectrophotometer. The alignment is facilitated by the use of two 2-inch x 2-inch white cards with 1-inch diameter holes cut in the center of each card. The cards are placed over each end of the absorption cell, and the cell is then aligned to provide maximum transmittance of the primary radiation from the mercury spectral lamp.

4.5 Compressed nitrogen gas of commercial grade or better.

4.6 Needle valve for primary control of nitrogen gas flow.

4.7 Flowmeter: Any calibrated flowmeter capable of measuring a nitrogen flow of 0.5 L/min is suitable.

4.8 Charcoal filter trap: A cylindrical tube, 1 inch in diameter (o.d.) and 6 inches in length, containing activated charcoal for adsorbing mercury and organics in the nitrogen gas stream is suitable.

4.9 Reduction-aeration sample cell: A 125-mL gas sparging bottle and a straight glass bubbling tube with an end-frit of a coarse porosity.

4.10 Variac autotransformer, or equivalent, capable of 20 volts output.

4.11 Silver wool, micro.

4.12 Chromel-A wire, 22-gauge, 3 feet.

4.13 Aeration tubing: Glass tubing is used for the passage of the mercury vapor from the gas sparging sample bottle to the silver-wool collection tube and then to the absorption cell. Tygon™ tubing is used for glass-to-glass connections as necessary.

4.14 The cold-vapor/amalgamation apparatus is assembled as shown via the schematic diagram in Figure 1A and the block diagram in Figure 1B. The cold-vapor/amalgamation system shown in Figure 1 is an open system where mercury vapor is passed through the absorption cell only once.

4.15 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, Tygon™ tubing connected to the exit port on the side of the absorption cell is used to vent mercury vapor into an exhaust hood.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): The water should be monitored for impurities.

5.2 Sulfuric acid (concentrated), H_2SO_4, reagent grade.

5.3 Sulfuric acid (0.5N), H_2SO_4: Prepare by carefully diluting 14.0 mL concentrated sulfuric acid to 1.0 L.

5.4 Nitric acid (concentrated), HNO_3, reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Hydrochloric acid (concentrated), HCl, reagent grade of low mercury content.

5.6 Stannous sulfate, $SnSO_4$, reagent grade.

5.7 Stannous sulfate solution: Add 100 g stannous sulfate to 1 L of 0.5N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. Stannous chloride may be used in place of stannous sulfate.

5.8 Stannous chloride, $SnCl_2 \cdot 2H_2O$, reagent grade.

5.9 Stannous chloride solution: Add 150 g stannous chloride to 300 mL of concentrated hydrochloric acid. After the stannous chloride has dissolved, dilute to 1 L with Type II water.

5.10 Sodium chloride, NaCl, reagent grade.

5.11 Hydroxylamine sulfate, $(NH_2OH)_2 \cdot 2H_2SO_4$, reagent grade.

5.12 Sodium chloride-hydroxylamine sulfate solution: Dissolve 120 g sodium chloride and 120 g hydroxylamine sulfate in Type II water and dilute to 1 L. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.13 Hydroxylamine hydrochloride, $NH_2OH \cdot HCl$, reagent grade.

5.14 Sodium chloride-hydroxylamine hydrochloride solution: Dissolve 120 g sodium chloride and 120 g hydroxylamine hydrochloride in Type II water and dilute to 1 L.

5.15 Potassium permanganate, $KMnO_4$, reagent grade.

5.16 Potassium permanganate, 5-percent (w/v) solution: Dissolve 50 g potassium permanganate in 1 L Type II water.

5.17 Potassium persulfate, $K_2S_2O_8$, reagent grade.

5.18 Potassium persulfate, 5-percent (w/v) solution: Dissolve 50 g potassium persulfate in 1 L Type II water.

5.19 Mercuric chloride, $HgCl_2$, reagent grade.

5.20 Mercury stock solution: Dissolve 0.1354 g mercuric chloride in 75 mL Type II water. Add 10 mL concentrated nitric acid and adjust the volume to 100.0 mL with Type II water (1 mL = 1 mg Hg). (A commercial 1000-mg/L atomic absorption standard may also be used as the mercury stock solution.)

5.21 Mercury working standards: Make successive dilutions of the mercury stock solution to obtain a working standard containing 0.01 µg/mL. This working standard and the dilutions of the mercury stock solution should be prepared fresh daily. Acidity of the working standards should be maintained at 0.15 percent nitric acid. This acid should be added to the flask before addition of the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected by making use of a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid. The suggested maximum holding times for these samples are 38 days in glass containers and 13 days in plastic containers.

7.0 PROCEDURE

7.1 Sample preparation (steam-bath digestion):

7.1.1 All glassware for sample digestions, sample dilutions, and standard preparations must be prewashed sequentially with an aqueous detergent solution, mineral acids, and Type II water.

7.1.2 Transfer a 50-mL sample aliquot to a tared, 125-mL Erlenmeyer flask. Add 5 mL concentrated sulfuric acid and 2.5 mL concentrated nitric acid. Thoroughly mix by hand-swirling after each addition. Add 15 mL of potassium permanganate solution. Thoroughly mix by hand-swirling. Sewage samples may require additional permanganate. While mixing by hand-swirling, add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 mL potassium persulfate solution and mix by hand-swirling. Cover the top of the flask with a watch glass. Heat for 2 hours on a steam bath maintained at a temperature of approximately 95°C. After cooling and immediately prior to analysis, add 6 mL sodium chloride-hydroxylamine hydrochloride solution or sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate in solution and the manganese dioxide particles adhering to the flask wall. Quantitatively transfer the sample solution to a 100-mL volumetric flask and dilute to calibrated volume with Type II water. Mix thoroughly and agitate by hand-swirling.

7.2 Standard preparation: Transfer appropriate aliquots of the mercury working standards to a series of 125-mL Erlenmeyer flasks. The aliquots must be selected to provide suitable calibration standards within the linear dynamic range of the instrument. Add Type II water to each flask to adjust the total volume to 50 mL and thoroughly mix by hand-swirling. Add 5 mL concentrated sulfuric acid and 2.5 mL concentrated nitric acid to each flask, mixing by hand-swirling after each addition. Add 15 mL potassium permanganate solution to each flask and allow to stand at least 15 minutes. Add 8 mL potassium persulfate solution to each flask and heat for 2 hours on the steam bath maintained at a temperature of approximately 95°C. After cooling and immediately prior to analysis, add 6 mL sodium chloride-hydroxylamine hydrochloride solution or sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate in solution and the manganese dioxide particles adhering to the flask wall. Quantitatively transfer the standard solutions to 100-mL volumetric flasks and dilute to calibrated volume with Type II water. Mix thoroughly and agitate by hand-swirling.

7.3 Analysis: Quantitatively transfer an appropriate aliquot of sample, standard, or reagent blank solution from the 100-mL volumetric flask to the 125-mL sparging bottle. Add Type II water to adjust the total volume to 100 mL. Add 5 mL stannous sulfate or stannous chloride solution. Ensure that the nitrogen purge gas flow is set between 500 and 600 mL/min and that the purge gas flow is directed through the bypass valve instead of through the aeration bubbler tube of the cold-vapor/amalgamation apparatus. Also, ensure that the exit end of the silver-wool collection tube is disconnected from the absorption cell. Connect the sparging bottle to the cold-vapor apparatus, and redirect the nitrogen purge gas flow through the aeration

apparatus, and redirect the nitrogen purge gas flow through the aeration bubbler tube for exactly 2 minutes. After the 2-minute concentration time, redirect the nitrogen purge gas flow through the bypass valve, and connect the exit end of the silver-wool collection tube to the absorption cell. After the nitrogen purge gas has been directed through the bypass valve for 1 minute, turn on the Variac autotransformer and strip-chart recorder. Initiate an atomic absorption measurement (maximum peak height) of 60 seconds duration; this measurement time may be pre-programmed with some spectrophotometers to provide a digital display of the maximum absorbance during this time interval. The mercury atomic absorption peak maximum should appear on the strip-chart within 45 seconds. When the atomic absorption peak has receded to 0.010 absorbance unit, turn off the Variac autotransformer and strip-chart recorder, and cool the outside of the silver-wool collection tube by a stream of air. When the mercury value exceeds the linear range of the calibration curve, the analysis must be repeated with smaller sample aliquots.

7.4 Construct a calibration curve by plotting the absorbance of a series of mercury standards versus micrograms of mercury. Determine the absorbance peak height of the unknown sample from the strip-chart or from the digital display of the atomic absorption spectrophotometer. Determine the mercury concentration value from the standard curve.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.7 Calculate mercury concentrations by (1) the method of standard additions or (2) from a calibration curve or (3) directly from the calibrated concentration readout display of the spectrophotometer. All dilution or concentration factors must be taken into account.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a reagent blank and three standards.

8.3 Dilute samples if their mercury concentrations are higher than that of the highest standard or if their mercury concentrations fall on the plateau of the calibration curve.

8.4 Analyze a minimum of one reagent blank per sample batch to determine if contamination or memory effects are occurring.

8.5 Analyze check standards after approximately every 6 samples.

8.6 Analyze one duplicate sample for every 10 samples.

8.7 Spiked samples or standard reference materials shall be periodically analyzed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analyses of all EP extracts, for all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Because of the lack of ruggedness demonstrated in an interlaboratory study, the accuracy and precision of the method has not been statistically determined.

10.0 REFERENCES

<<A>>Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 2nd Edition, July 1982, U. S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

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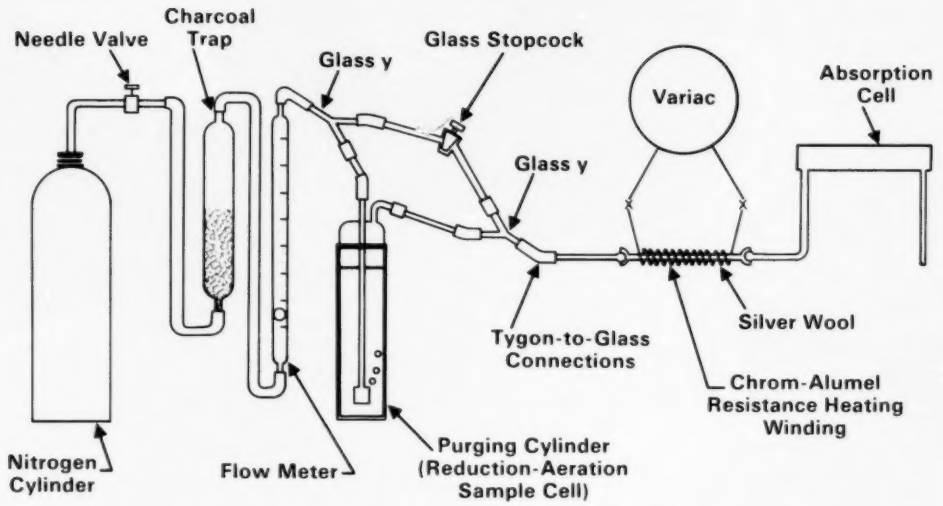

Figure 1A. Schematic diagram of the amalgamation CV-AAS system.

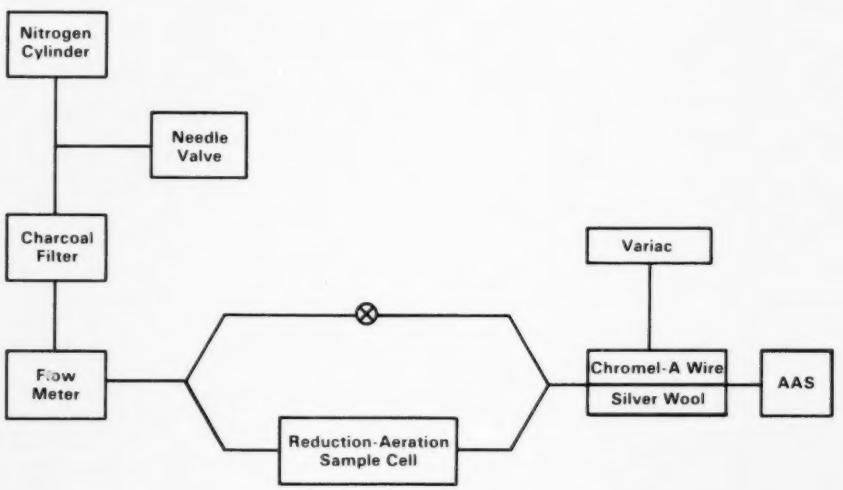

Figure 1B. Block diagram of the amalgamation CV-AAS system.

APPENDIX B

METHOD 7471 (Proposed Revision)

MERCURY (MANUAL AMALGAMATION COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is a cold-vapor atomic absorption procedure recommended for measuring low concentrations of total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate digestion step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the samples must be prepared according to one of the procedures discussed in this method.

2.2 This method, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state, aerated from solution by a nitrogen purge, and concentrated by amalgamation on silver wool. The amalgamated mercury is thermally volatilized from the silver wool by resistance heating of a nichrome wire wrapped around Pyrex tubing containing the silver wool and is then carried by the nitrogen purge gas into the glass absorption cell for the atomic absorption measurement. The analytical calibration curve is based on the maximum absorbance (peak height) determined for each measurement.

2.3 The typical instrument detection limit for this method is approximately 1 ng (5 ng/g based on a 0.2-g sample weight).

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. In a single-laboratory study, concentrations as high as 2 mg of sulfide as sodium sulfide per 0.2-g sample did not interfere with the recovery of mercury from NBS-SRM 1646 (Estuarine sediment).

3.2 Copper has been reported to interfere. In a single-laboratory study, copper concentrations as high as 1 mg per 0.2-g sample generally had no effect on the recovery of mercury from NBS-SRM 1646 (Estuarine sediment). However, in an interlaboratory study, low recoveries of spiked inorganic mercury in a composite incinerator fly ash sample containing 1 mg of copper were obtained.

3.3 High levels of chloride in seawaters, brines, and industrial effluents have been reported to interfere; however, in a single-laboratory study, concentrations as high as 30 mg sodium chloride per 0.2-g sample had no effect on recovery of mercury from NBS-SRM 1646 (Estuarine sediment). Care must be taken to ensure that free chlorine is absent before the mercury

is reduced and swept into the absorption cell. This may be accomplished by using an excess of hydroxylamine sulfate or hydroxylamine hydrochloride reagent (25 mL). In addition, the dead air space in the reduction-aeration sample cell must be purged before adding stannous sulfate or stannous chloride. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this digestion method in previous studies.

3.4 Certain volatile organic materials may absorb at the 253.7 nm wavelength; however, no nonspecific absorption interferences were observed for NBS-SRM 1645 (River Sediment) spiked with benzene and methyl ethyl ketone.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit having an open sample atomization area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the spectrophotometric measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange, variable-speed recorder with a one-second time constant that is compatible with the photometric detection system is suitable.

4.4 Absorption cell: A cylindrical glass cell having entrance and exit ports on the side and quartz end-windows to transmit ultraviolet radiation is suitable. A cylindrical cell, 1 inch in diameter (o.d.) and 6 inches in length, has been found to be an appropriate geometry. The absorption cell is strapped to a burner head assembly for convenient positioning and for two-dimensional alignment in the optical path of the sample atomization area of the atomic absorption spectrophotometer. The alignment is facilitated by the use of two 2-inch x 2-inch white cards with 1-inch diameter holes cut in the center of each card. The cards are placed over each end of the absorption cell, and the cell is then aligned to provide maximum transmittance of the primary radiation from the mercury spectral lamp.

4.5 Compressed nitrogen gas of commercial grade or better.

4.6 Needle valve for primary control of nitrogen gas flow.

4.7 Flowmeter: Any calibrated flowmeter capable of measuring a nitrogen flow of 0.5 L/min is suitable.

4.8 Charcoal filter trap: A cylindrical tube, 1 inch in diameter (o.d.) and 6 inches in length, containing activated charcoal for adsorbing mercury and organics in the nitrogen gas stream is suitable.

4.9 Reduction-aeration sample cell: A 125-mL gas sparging bottle and a straight glass bubbling tube with an end-frit of a coarse porosity.

4.10 Variac autotransformer, or equivalent, capable of 20 volts output.

4.11 Silver wool, micro.

4.12 Chromel-A wire, 22-gauge, 3 feet.

4.13 Aeration tubing: Glass tubing is used for the passage of the mercury vapor from the gas sparging sample bottle to the silver-wool collection tube and then to the absorption cell. Tygon™ tubing is used for glass-to-glass connections as necessary.

4.14 The cold-vapor/amalgamation apparatus is assembled as shown via the schematic diagram in Figure 1A and the block diagram in Figure 1B. The cold-vapor/amalgamation system shown in Figure 1 is an open system where mercury vapor is passed through the absorption cell only once.

4.15 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, Tygon™ tubing connected to the exit port on the side of the absorption cell is used to vent mercury vapor into an exhaust hood.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): The water should be monitored for impurities.

5.2 Nitric acid (concentrated), HNO_3, reagent grade.

5.3 Hydrochloric acid (concentrated), HCl, reagent grade.

5.4 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated hydrochloric acid to one volume of concentrated nitric acid.

5.5 Sulfuric acid (concentrated), H_2SO_4, reagent grade.

5.6 Sulfuric acid (0.5N), H_2SO_4: Prepare by carefully diluting 14.0 mL concentrated sulfuric acid to 1 liter.

5.7 Stannous sulfate, $SnSO_4$, reagent grade.

5.8 Stannous sulfate solution: Add 25 g stannous sulfate to 250 mL of 0.5N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. Stannous chloride may be used in place of stannous sulfate.

5.9 Stannous chloride, $SnCl_2 \cdot 2H_2O$, reagent grade.

5.10 Stannous chloride solution: Add 150 g stannous chloride to 300 mL of concentrated hydrochloric acid. After the stannous chloride has dissolved, dilute to 1 L with Type II water.

5.11 Sodium chloride, NaCl, reagent grade.

5.12 Hydroxylamine sulfate, $(NH_2OH)_2 \cdot 2H_2SO_4$, reagent grade.

5.13 Sodium chloride-hydroxylamine sulfate solution: Dissolve 120 g sodium chloride and 120 g hydroxylamine sulfate in Type II water and dilute to 1 L. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.14 Hydroxylamine hydrochloride, $NH_2OH \cdot HCl$, reagent grade.

5.15 Sodium chloride-hydroxylamine hydrochloride solution: Dissolve 120 g sodium chloride and 120 g hydroxylamine hydrochloride in Type II water and dilute to 1 L.

5.16 Potassium permanganate, $KMnO_4$, reagent grade.

5.17 Potassium permanganate, 5-percent solution (w/v): Dissolve 50 g potassium permanganate in 1 L Type II water.

5.18 Mercuric chloride, $HgCl_2$, reagent grade.

5.19 Mercury stock solution: Dissolve 0.1354 g mercuric chloride in 75 mL Type II water. Add 10 mL concentrated nitric acid and adjust the volume to 100.0 mL with Type II water (1 mL = 1 mg Hg). (A commercial 1000-mg/L atomic absorption standard may also be used as the mercury stock solution.)

5.20 Mercury working standards: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.01 µg/mL. This working standard and the dilutions of the mercury stock solution should be prepared fresh daily. Acidity of the working standards should be maintained at 0.15 percent nitric acid. This acid should be added to the flask before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected by making use of a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Nonaqueous samples shall be refrigerated and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation (steam-bath digestion):

7.1.1 All glassware for sample digestions, sample dilutions, and standard preparations must be prewashed sequentially with an aqueous detergent solution, mineral acids, and Type II water.

7.1.2 Weigh a 0.2-g portion of wet sample into a tared, 125-mL Erlenmeyer flask. Add 5 mL Type II water and 5 mL aqua regia. Mix by hand-swirling. Cover the top of the flask with a watch glass. Heat for 2 minutes on a steam bath maintained at a temperature of approximately 95°C. After cooling, add 50 mL Type II water and 15 mL potassium permanganate solution. Mix thoroughly by hand-swirling. Heat for 30 minutes on the steam bath maintained at a temperature of approximately 95°C. After cooling and immediately prior to analysis, add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution or sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate in solution and the manganese dioxide particles adhering to the flask wall. Quantitatively transfer the sample solution to a 100-mL volumetric flask and dilute to calibrated volume with Type II water. Mix thoroughly and agitate by hand-swirling.

7.1.3 Standard preparation: Transfer appropriate aliquots of the mercury working standards to a series of 125-mL Erlenmeyer flasks. The aliquots must be selected to provide suitable calibration standards within the linear dynamic range of the instrument. Add Type II water to each flask to adjust the total volume to 10 mL. Add 5 mL aqua regia and thoroughly mix by hand-swirling. Cover the top of the flask with a watch glass. Heat for 2 minutes on the steam bath maintained at a temperature of 95°C. After cooling, add 50 mL Type II water and 15 mL potassium permanganate solution. Mix thoroughly by hand-swirling. Heat on the steam bath for 30 minutes. After cooling and immediately prior to analysis, add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution or sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate in solution and the manganese dioxide particles adhering to the flask wall. Quantitatively transfer the sample solution to a 100-mL volumetric flask and dilute to calibrated volume with Type II water. Thoroughly mix and agitate by hand-swirling.

7.2 Alternate sample preparation (autoclave digestion):

7.2.1 All glassware for sample digestions, sample dilutions, and standard preparations must be prewashed sequentially with a detergent solution, mineral acids, and then Type II water.

7.2.2 Weigh a 0.2-g portion of wet sample into a tared, 125-mL Erlenmeyer flask. Add 5 mL Type II water, 5 mL concentrated sulfuric acid, 2 mL concentrated nitric acid, and 5 mL potassium permanganate solution. Mix thoroughly by hand-swirling. Cover the top of the flask with a piece of aluminum foil. Autoclave the sample at 121°C and 15

psi for 15 minutes. After cooling and immediately prior to analysis, add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution or sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate in solution and the manganese dioxide particles adhering to the flask wall. Quantitatively transfer the sample solution to a 100-mL volumetric flask and dilute to calibrated volume with Type II water. Mix thoroughly and agitate by hand-swirling.

7.2.3 Standard preparation: Transfer appropriate aliquots of the mercury working standards to a series of 125-mL Erlenmeyer flasks. The aliquots must be selected to provide suitable calibration standards within the linear dynamic range of the instrument. Add Type II water to adjust the total volume to 10 mL in each flask. Add 5 mL Type II water, 5 mL concentrated sulfuric acid, 2 mL concentrated nitric acid, and 5 mL potassium permanganate solution. Thoroughly mix by hand-swirling. Cover the top of each flask with a piece of aluminum foil. Autoclave the standards at 121°C and 15 psi for 15 minutes. After cooling and immediately prior to analysis, add 6 mL sodium chloride-hydroxylamine hydrochloride solution to reduce excess permanganate in solution and the manganese dioxide particles adhering to the flask wall. Quantitatively transfer the standard solutions to 100-mL volumetric flasks and dilute to calibrated volume with Type II water. Mix thoroughly and agitate by hand-swirling.

7.3 Analysis: Quantitatively transfer an appropriate aliquot of sample, standard, or reagent blank solution from the 100-mL volumetric flask to the 125-mL sparging bottle. Add Type II water to adjust the total volume to 100 mL. Add 5 mL stannous sulfate or stannous chloride solution. Ensure that the nitrogen purge gas flow is set between 500 and 600 mL/min and that the purge gas flow is directed through the bypass valve instead of through the aeration bubbler tube of the cold-vapor/amalgamation apparatus. Also, ensure that the exit end of the silver-wool collection tube is disconnected from the absorption cell. Connect the sparging bottle to the cold-vapor apparatus, and redirect the nitrogen purge gas flow through the aeration bubbler tube for exactly 2 minutes. After the 2-minute concentration time, redirect the nitrogen purge gas flow through the bypass valve, and connect the exit end of the silver-wool collection tube to the absorption cell. After the nitrogen purge gas has been directed through the bypass valve for 1 minute, turn on the Variac autotransformer and strip-chart recorder. Initiate an atomic absorption measurement (maximum peak height) of 60 seconds duration; this measurement time may be pre-programmed with some spectrophotometers to provide a digital display of the maximum absorbance during this time interval. The mercury atomic absorption peak maximum should appear on the strip-chart within 45 seconds. When the atomic absorption peak has receded to 0.010 absorbance unit, turn off the Variac autotransformer and strip-chart recorder, and cool the outside of the silver-wool collection tube by a stream of air. When the mercury value exceeds the linear range of the calibration curve, the analysis must be repeated with smaller sample aliquots.

7.4 Construct a calibration curve by plotting the absorbance of a series of mercury standards versus micrograms of mercury. Determine the

absorbance peak height of the unknown sample from the strip-chart or from the digital display of the atomic absorption spectrophotometer. Determine the mercury concentration value from the standard curve.

7.5 Analyze, by the method of standard additions, all samples analyzed as part of a delisting petition and all samples that suffer from matrix interferences.

7.6 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.7 Calculate mercury concentrations by (1) the method of standard additions or (2) from a calibration curve or (3) directly from the calibrated concentration readout display of the spectrophotometer. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a reagent blank and three standards.

8.3 Dilute sample digests if their mercury concentrations are higher than that of the highest standard or if their mercury concentrations fall on the plateau of the calibration curve.

8.4 Analyze a minimum of one reagent blank per sample batch to determine if contamination or memory effects are occurring.

8.5 Analyze check standards after approximately every 6 samples.

8.6 Analyze one duplicate sample for every 10 samples.

8.7 Spiked samples or standard reference materials shall be periodically analyzed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Because of the lack of ruggedness demonstrated in an interlaboratory study, the accuracy and precision of the method has not been statistically determined.

10.0 REFERENCES

<<A>>Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 2nd Edition, July 1982, U. S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

<<B>>Messman, J. D., M. E. Churchwell, R. L. Livingston, and D. L. Sgontz. 1986. Evaluation and Testing of EPA Protocols for SW-846 Methods 7470 and 7471. Final Report. U.S. Environmental Protection Agency.

<<C>>Churchwell, M. E., R. L. Livingston, D. L. Sgontz, J. D. Messman, and W. F. Beckert. 1988 (in press). Environment International.

<<D>>Youden, W. J., and E. H. Steiner. Statistical Manual of the AOAC. Association of Official Analytical Chemists, Arlington, Virginia, 1975. 88 pp.

<<E>>Gebhart, J. E., J. D. Messman, and G. F. Wallace. 1987. Interlaboratory Evaluation of SW-846 Methods 7470 and 7471 for the Determination of Mercury in Environmental Samples. Final Report. U.S. Environmental Protection Agency.

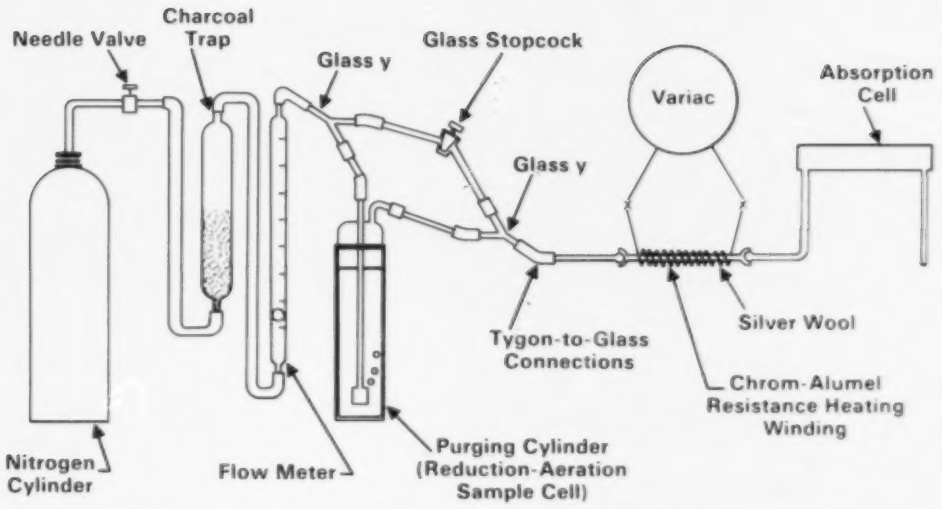

Figure 1A. Schematic diagram of the amalgamation CV-AAS system.

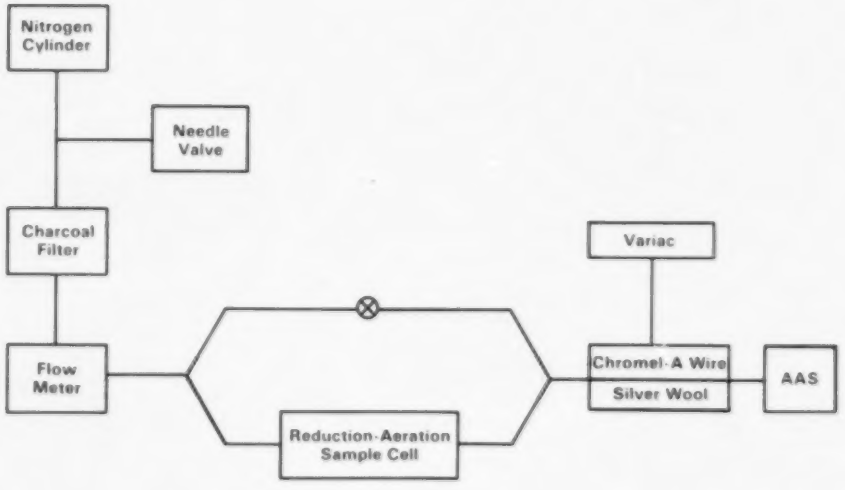

Figure 1B. Block diagram of the amalgamation CV-AAS system.

APPENDIX C

PHASE III - OPTION A SAMPLE LIST

Option A of Phase III specifies a sample mix of a reference sediment, two solid waste materials, and three aqueous samples. The two solid waste materials and two of the aqueous samples are designated for mercury predigestion spikes. Based on duplicates of each sample, the total sample mix represents 16 samples. These 16 samples are listed below:

#1	Canadian reference sediment MESS-1
#2	Duplicate of #1
#3	Incinerator fly ash
#4	Duplicate of #3
#5	Incinerator fly ash spiked with 100 ng of inorganic mercury
#6	Duplicate of #5
#7	Municipal sewage sludge
#8	Duplicate of #7
#9	Municipal sewage sludge spiked with 100 ng of organic mercury
#10	Duplicate of #9
#11	Ground water
#12	Duplicate of #11
#13	Waste water spiked with 50 ng of inorganic mercury
#14	Duplicate of #13
#15	One percent (v/v) HNO_3 spiked with 25 ng of inorganic mercury
#16	Duplicate of #15

APPENDIX D

PHASE III - OPTION B SAMPLE LIST

Option B of Phase III specifies a sample mix of a reference sediment, two solid waste materials, and three aqueous samples. The two solid waste materials and two of the aqueous samples are designated for mercury predigestion spikes. Based on three replicates of each sample, the total sample mix represents 24 samples. These 24 samples are listed below:

#1	Canadian reference sediment MESS-1
#2	Duplicate of #1
#3	Triplicate of #1
#4	Incinerator fly ash
#5	Duplicate of #4
#6	Triplicate of #4
#7	Incinerator fly ash spiked with 37.5 ng of inorganic mercury plus 1 mg copper
#8	Duplicate of #7
#9	Triplicate of #7
#10	Municipal sewage sludge
#11	Duplicate of #10
#12	Triplicate of #10
#13	Municipal sewage sludge spiked with 50 ng of organic mercury
#14	Duplicate of #13
#15	Triplicate of #13
#16	Ground water
#17	Duplicate of #16
#18	Triplicate of #16
#19	Waste water spiked with 25 ng of inorganic mercury
#20	Duplicate of #19
#21	Triplicate of #19
#22	One percent (v/v) HNO_3 spiked with 25 ng of inorganic mercury
#23	Duplicate of #22
#24	Triplicate of #22

APPENDIX E

INTERLABORATORY DATA FOR REVISED METHODS 7470 AND 7471

TABLE E-1. SUMMARY OF CALIBRATION AND REAGENT BLANK VALUES FOR PHASE II ANALYSES

Laboratory Identification Number	Method 7470		Method 7471	
	Slope[a] (abs/ng)	Reagent Blank (abs)	Slope[a] (abs/ng)	Reagent Blank (abs)
949	0.0035	0.040	- - -	- - -
950	0.0037	0.007	0.0048	0.011
951	- - -	- - -	- - -	- - -
952	0.0038	0.004	0.0038	0.006
953	0.0041	0.013	0.0041	0.019
954	0.0015	0.006	0.0015	0.006
955	0.0011	0.120	0.0006	0.086
956	0.0008	0.008	0.0008	0.003
957	- - -	- - -	- - -	- - -
958	0.0032	0.054	- - -	- - -
959	0.0056	0.014	0.0025	0.011
960	0.0010	0.001	0.0010	0.001
961	0.003	0.005	- - -	- - -
962	0.0018	0.004	0.0016	0.001
963	0.0047	0.117	0.0033	0.602
964	0.0036	0.122	0.0036	0.122
965	0.0036	0.258	0.0001	0.644
966	0.0011	0.003	0.0011	0.003

[a] Slope of calibration curve (typical slope for Battelle testing is 0.005 abs/ng).

TABLE E-2. SUMMARY OF CALIBRATION AND REAGENT BLANK VALUES FOR PHASE III ANALYSES

Laboratory Identification Number	Method 7470		Method 7471	
	Slope[a] (abs/ng)	Reagent Blank (abs)	Slope[a] (abs/ng)	Reagent Blank (abs)
Option A				
955	0.0036	0.021	0.0030	0.025
957	0.0021	0.027	0.0017	0.020
962	0.0018	0.010	0.0023	0.012
964	0.004	0.014	0.004	0.004
965	0.0029	0.046	0.0035	0.054
Option B				
950	0.0036	0.006	0.0034	0.008
952	0.0056	0.008	0.0028	0.008
953	0.0036	-0.004	0.0065	0.003
954	0.0019	0.014	0.0024	0.075
966	0.0010	0.002	0.0010	0.002

[a] Slope of calibration curve (typical slope for Battelle testing is 0.005 abs/ng).

TABLE E-3. SUMMARY OF MERCURY CONCENTRATIONS IN GROUND WATER[a]

Laboratory Identification Number	Mercury Concentration, ng			Mean	Std. Dev.
Option A	#11	#12			
955	2	3		2	0.71
957	1	<1		≤1	- -
962	4	8		6	2.8
964	7150	8700		-	- -
965	5	8		6	2.1
Option B	#16	#17	#18		
950	<10	<10	<10	<10	- -
952	6	11	6	8	2.9
953	5	4	4	4	0.58
954	<1	<1	1	≤1	- -
966	51	44	42	-	- -

[a] Endogenous mercury concentration - not detectable (<1 ng); based on 20-mL sample aliquot.

TABLE E-4. SUMMARY OF MERCURY CONCENTRATIONS IN WASTE WATER[a] SPIKED WITH INORGANIC MERCURY

Laboratory Identification Number	Mercury Concentration, ng			Percent Recovery	
				Mean	Std. Dev.
Option A	#13	#14			
955	37	51		88	20
957	80	84		160	5.7
962	115	100		220	21
964	9850	8600		- -	- -
965	32	45		77	18
Option B	#19	#20	#21		
950	59	62	62	240	6.9
952	346000	300	150	- -	- -
953	23	22	22	89	2.3
954	48	42	34	160	28
966	27	27	27	110	0

[a] Endogenous mercury concentration - not detectable (<1 ng); based on 20-mL sample aliquot.
Option A spike: 50 ng Hg; target mercury concentration = 50 ng.
Option B spike: 25 ng Hg; target mercury concentration = 25 ng.

TABLE E-5. SUMMARY OF MERCURY CONCENTRATIONS IN DILUTE NITRIC ACID[a] SPIKED WITH INORGANIC MERCURY

Laboratory Identification Number	Mercury Concentration, ng			Percent Recovery	
				Mean	Std. Dev.
Option A	#15	#16			
955	4	5		18	2.8
957	22	22		88	0
962	40	26		130	40
964	8650	5950		- -	- -
965	29	16		90	37
Option B	#22	#23	#24		
950	42	29	20	120	44
952	40	22	18	110	47
953	2	2	3	9	2.3
954	19	14	27	80	26
966	24	21	26	95	10

[a] Endogenous mercury concentration - not detectable (<1 ng); based on 20-mL sample aliquot.
Option A and B spikes: 25 ng Hg; target mercury concentration = 25 ng.

TABLE E-6. SUMMARY OF MERCURY CONCENTRATIONS IN MARINE SEDIMENT MESS-1[a]

Laboratory Identification Number	Mercury Concentration, mg/kg			Percent Recovery	
				Mean	Std. Dev.
Option A	#1	#2			
955	0.19	0.21		120	8.3
957	0.18	0.17		100	4.1
962	0.17	0.18		100	4.1
964	0.77	0.28		- -	- -
965	0.22	0.24		140	8.3
Option B	#1	#2	#3		
950	0.31	0.18	0.23	140	41
952	0.12	0.12	0.093	66	6.8
953	0.14	0.20	0.14	94	20
954	0.09	0.26	0.42	150	97
966	0.19	0.18	0.18	110	3.4

[a] Reference mercury concentration = 0.171 ± 0.014 mg/kg.

TABLE E-7. SUMMARY OF MERCURY CONCENTRATIONS IN INCINERATOR FLY ASH[a]

Laboratory Identification Number	Mercury Concentration, mg/kg			Mean	Std. Dev.
Option A	#3	#4			
955	0.037	0.014		0.026	0.016
957	<0.005	<0.005		<0.005	- - -
962	0.013	0.018		0.016	0.0035
964	0.43	0.14		- - -	- - -
965	0.033	0.043		0.038	0.0071
Option B	#4	#5	#6		
950	<0.05	<0.05	0.075	0.058	0.014
952	0.017	0.025	0.029	0.024	0.0061
953	0.079	0.10	0.026	0.068	0.038
954	0.22	0.18	0.20	0.20	0.020
966	0.014	0.014	0.028	0.019	0.0081

[a] Endogenous mercury concentration - not detectable (<0.005 mg/kg).

TABLE E-8. SUMMARY OF MERCURY CONCENTRATIONS IN INCINERATOR FLY ASH[a] SPIKED WITH INORGANIC MERCURY

Laboratory Identification Number	Mercury Concentration, mg/kg			Percent Recovery	
				Mean	Std. Dev.
Option A	#5	#6			
955	<0.005	0.075		8	10
957	0.55	0.62		120	10
962	0.40	0.41		81	1.4
964	2.62	1.09		- -	- -
965	0.49	0.42		91	10
Option B	#7	#8	#9		
950	<0.05	<0.05	<0.05	<26	- -
952	0.019	0.029	0.028	13	2.9
953	0.062	0.050	0.033	25	7.7
954	0.16	0.13	0.12	72	11
966	0.058	0.17	0.094	56	30

[a] Option A spike: 100 ng Hg; target mercury concentration = 0.50 mg/kg. Option B spikes: 37.5 ng Hg + 1 mg Cu; target mercury concentration = 0.19 mg/kg.

TABLE E-9. SUMMARY OF MERCURY CONCENTRATIONS IN MUNICIPAL SEWAGE SLUDGE[a]

Laboratory Identification Number	Mercury Concentration, mg/kg			Percent Recovery	
				Mean	Std. Dev.
Option A	#7	#8			
955	1.40	1.30		96	5.1
957	2.04	1.51		130	27
962	1.08	1.07		77	0.51
964	2.26	3.42		- -	- -
965	0.80	0.90		61	5.1
Option B	#10	#11	#12		
950	1.64	1.49	1.45	110	7.2
952	1.23	1.21	2.02	110	32
953	0.20	0.24	0.11	13	4.8
954	1.55	1.70	1.30	110	14
966	1.14	1.41	1.91	110	28

[a] Target mercury concentration = 1.4 mg/kg.

TABLE E-10. SUMMARY OF MERCURY CONCENTRATIONS IN MUNICIPAL SEWAGE SLUDGE[a] SPIKED WITH ORGANIC MERCURY

Laboratory Identification Number	Mercury Concentration, mg/kg			Percent Recovery	
				Mean	Std. Dev.
Option A	#9	#10			
955	2.22	0.92		83	48
957	3.19	2.76		160	16
962	1.90	1.72		95	6.7
964	2.53	3.60		- -	- -
965	1.00	1.05		54	1.9
Option B	#13	#14	#15		
950	1.76	1.74	1.66	100	3.2
952	1.39	1.65	1.52	92	7.6
953	0.17	0.25	0.15	12	3.2
954	2.30	1.75	2.55	130	25
966	1.70	1.87	1.77	110	5.2

[a] Option A spike: 100 ng Hg; target mercury concentration = 1.9 mg/kg.
Option B spike: 50 ng Hg; target mercury concentration = 1.65 mg/kg.